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A First Principles Investigation of Proton Chemistry in Perovskite-Type Oxides

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A First Principles Investigation of Proton Chemistry
in Perovskite-Type Oxides

by

Tania Allison Tauer
B.S., University of Virginia, 2008

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado, Boulder in partial fulfillment
of the requirement for the degree of
Doctor of Philosophy
Department of Chemical and Biological Engineering
2013
This thesis entitled:
A First Principles Investigation of Proton Chemistry in Perovskite-Type Oxides

written by Tania Allison Tauer

has been approved for the Department of Chemical and Biological Engineering

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Date: November 18, 2013
The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Abstract

Tauer, Tania A. (Ph.D. Chemical Engineering)
Department of Chemical and Biological Engineering, University of Colorado Boulder
A First Principles Investigation of Proton Chemistry in Perovskite-Type Oxides
Thesis directed by J. Will Medlin

Certain acceptor-doped perovskite-type oxides show significant promise for deployment into a number of electrochemical device applications, including fuel cells, batteries, and electrolyzers, owing to their rapid proton conductivities at high temperatures. However, limitations in bulk material hydration and slow grain boundary conductivities have reduced the viability of these materials in intermediate temperatures applications. This thesis work uses density functional theory to gain a fundamental understanding of proton and defect chemistry within various perovskite environments in order to identify strategies to increase proton concentration and improve overall proton conductivity.

First, material hydration was probed within yttrium-doped barium cerate (BCY) to examine how the thermodynamics of material hydration are influenced by dopant concentration. A model was derived from solely first principle techniques to describe hydration within BCY as a function of dopant concentration, temperature, and partial pressure of water. The resulting model can be used to screen for favorable perovskite-dopant combinations with enhanced hydration capabilities.

Next, defect segregation was investigated in the more complex interfacial environment to probe the origin of low proton conductivity across perovskite grain boundaries (GB). The results of this study suggest that screening for perovskite-dopant
combinations with strong dopant-oxygen bond strengths may reduce the segregation of dopant ions and oxygen vacancies to the GB interface, mitigating the development of a positive GB core and enhancing proton conduction across the GB.

Finally, proton stability was assessed at various interfacial regions within the perovskite material. An examination of proton adsorption at the BaZrO$_3$-vacuum interface reveals a destabilization of protons in the first subsurface layer of the perovskite, yielding a potential barrier for proton diffusion into and out of the perovskite membrane. An electronic analysis of oxygen ions indicates that the oxygen p-band center influences proton adsorption strength. This p-band center model was shown to accurately describe adsorption trends within bulk BCY as well. An analysis of proton adsorption at BaZrO$_3$-metal heterointerfaces displayed a stabilization of protons in the near heterointerfacial environment compared to the BaZrO$_3$-vacuum surface. This stabilization reduces the barrier for proton diffusion near the perovskite interface and likely leads to increased proton concentrations at the perovskite-metal heterointerface.
To Grandpa Webber
Acknowledgements

This thesis work would not have been possible without the guidance and support of numerous individuals. First, I would like to thank my advisor, Will Medlin, who has been both a phenomenal advisor and mentor over the past 5 years. Will has offered me continual support throughout this journey, through both the highs and lows that graduate school often entails. He is always a strong advocate for his students and has helped guide me to become a stronger engineer and scientist. I have learned an enormous amount from Will during this time as his student, and I am truly grateful for the opportunity to work with him. I would also like to thank my thesis committee, Profs. Dan Schwartz, Charles Musgrave, Se-Hee Lee, and Ryan O’Hayre, for their helpful criticisms and feedback throughout the progression of this thesis work.

I have also been grateful to receive help and support from a number of collaborators. I have had the distinct pleasure of working with the Renewable Energy Materials Research Science and Engineering Center (REMRSEC) at the Colorado School of Mines under the direction of Ryan O’Hayre. Ryan has been an unparalleled resource over the course of this thesis, providing his extensive expertise and insights into this work. I would also like to thank the fellow students within the REMRSEC as well as the other mentors, Annette Bunge, Jianhua Tong, and Colin Wolden, who have offered much guidance and feedback during our bi-weekly meetings. I feel lucky to have had the unique experience of working with such diverse and talented group of researchers at the Colorado School of Mines.

This thesis also would not have been possible without the financial support of REMRSEC, which was funded by the National Science Foundation (Award DMR-0820518). The computational research was supported in part by the Golden Energy Computing Organization at the Colorado School of Mines using resources acquired with financial assistance
from the National Science Foundation and the National Renewable Energy Laboratory. Additional computational resources were provided by NSF-MRI Grant CNS-0821794, MRI-Consortium: Acquisition of a Supercomputer by the Front Range Computing Consortium (FRCC), with additional support from the University of Colorado and NSF sponsorship of the National Center for Atmospheric Research. We also acknowledge supercomputing time at the Center for Nanoscale Materials at Argonne National Laboratory, supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract no. DE-AC02-06CH11357.

Additionally, I would like to thank every member of the Medlin group that I have had the pleasure of working with over the past 5 years. I have been truly fortunate to work with such an amazing, intelligent, fun, and outgoing group. You all made it enjoyable to come to work everyday, and I can’t imagine ever finding a better group of colleagues. I would particularly like to thank Meghana Rangan, Simon Pang, and Matt Montemore, who helped to train me and offer me additional insights into the computational theory of my work. I would also like to acknowledge Mike Griffin and Troy Gould, who embarked on this crazy journey with me 5 years ago, and Carolyn Schoenbaum, who has been my confidant and steadfast friend since joining the Medlin group.

Finally, I would like to thank my friends and family, without whom I would not have been able to accomplish this feat. To Mark, thank you for your unwavering love and encouragement throughout the past 5 years. You have helped me achieve more than what I thought possible and have made life more fun and enjoyable throughout. I am truly lucky to have you in my life. To my friends, thank you for the ski trips, backpacking adventures, IM championships, game nights, soccer games, softball tournaments, and cookouts. Without you this
road would have been not nearly as tolerable. You will forever be my Boulder family. To my parents, Tom and Pam, thank you for always believing I could do anything, for pushing me to be my best, and supporting me through my hardships. I would not be who I am today without your love and guidance, not only over the last 5 years, but for the past 27 years. Thank you.
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CHAPTER I

INTRODUCTION AND BACKGROUND

1.0 Overview

Recent interest in developing a sustainable energy economy has led to the research and development of new energy storage and conversion technologies. Among them, fuel cells have garnered great attention for their potential use in transport applications, as a means to reduce reliance on conventional liquid fuels, and storage applications, in an effort to generate clean and reliable electricity.\textsuperscript{1-4} These electrochemical devices use a combination of catalyst electrodes and electrolyte membranes to convert chemical energy into electricity.\textsuperscript{5,6} While fuel cells have higher theoretical efficiencies than traditional combustion allows,\textsuperscript{7,8} their operating efficiencies are limited by numerous inefficiencies within the devices, including low conductivities within the ion conducting membranes and slow catalytic kinetics.\textsuperscript{9,10} The work done for this thesis addresses the former inefficiency by exploring ways to improve proton conductivities in a common class of proton conducting materials, perovskite oxides.
1.1 Introduction to Fuel Cells

Fuel cells are devices that convert chemical energy into electricity through a series of electrochemical reactions. A basic fuel cell is comprised of three components: an anode, a cathode, and an electrolyte membrane. The anode and cathode are electrodes that provide surfaces for the electrochemical reactions to take place.\textsuperscript{5,6} While these reactions are often quite complex and motivate an entire field of research in and of themselves, they can be broken down into two types of reactions. An oxidation reaction takes place on the anode to produce electrons, while a reduction reaction occurs at the cathode surface and consumes electrons.\textsuperscript{11} The electrolyte membrane is comprised of an electron impermeable material and acts to separate the two electrodes within the device. The high electrical resistance of the electrolyte forces electrons generated from the anode to travel through an external circuit to create electricity before being consumed in the reduction reaction on the cathode.\textsuperscript{12,13}

There are many types of fuel cells currently in development, each of which are distinguished by the type of electrolyte material incorporated into the device. This choice of material dictates the fuel required, operating temperature, power output, and ultimately the application for each type of fuel cell.\textsuperscript{2,14} Figure 1.1 depicts one of the simplest fuel cell types, the proton exchange membrane fuel cell (PEMFC). In this device, hydrogen reacts on the anode and splits into an electron and a proton. The proton travels through the electron-impermeable proton exchange membrane, while the electron is forced through an external circuit, creating electricity. Oxygen, in the form of air, is flowed into the opposite side of the device where it reacts with the proton and electron on the cathode surface to produce pure water.\textsuperscript{13,15}

Since its invention in the early 1960’s, the PEMFC has been developed for transportation, stationary, and portable applications due to a wide range of attractive
attributes.\textsuperscript{16,17} In particular, its high power density and quick start-up time make it an ideal candidate to replace combustion engines in cars and trucks.\textsuperscript{2} Traditionally, PEMFCs have incorporated an aqueous-based polymer electrolyte to facilitate proton transfer from the anode to the cathode. Within these systems, the humidity required to ensure sufficient proton conductivities limits operating temperatures to below 100°C to prevent the evaporation of the water within the electrolyte.\textsuperscript{10,18} Recent advancements in material composition have extended this temperature range up to about 140°C.\textsuperscript{19,20} However, these low temperatures still result in slow kinetics of the chemical reactions within the PEMFC, so expensive precious metal catalyst must be incorporated into the device to speed up these reactions.\textsuperscript{21} New research is currently being pursued to try to identify and develop new proton conducting materials that operate at intermediate (200-400°C) and high (400-1000°C) temperatures in an effort to reduce the amount of catalyst required for fuel cell operation and ultimately decrease the cost of these devices.\textsuperscript{22}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Proton Exchange Membrane (PEM) Fuel Cell.} In PEMFCs, hydrogen reacts on the anode surface to form a proton and electron. The proton travels through the proton conducting electrolyte membrane, while the electron travels through an external circuit,
producing electricity. The protons and electrons react with oxygen (in form of air) on the cathode surface to produce water.

1.2 Proton Conducting Materials

Proton conducting materials for fuel cell applications traditionally fall into two classes of materials: low temperature liquids and polymers and high temperature solid ceramics. The specific chemistries of each class of material dictate the optimal temperature ranges at which these proton conductors operate. Liquid electrolytes, such as H₃PO₄ used in phosphoric acid fuel cells, exhibit amongst the highest proton conductivities of any known material due to their high density and flexibility of hydrogen bonds. However, low temperature liquid electrolytes are not commonly incorporated into fuel cells due to lower power output and electrolyte instability. In polymer electrolytes, the presence of liquid water is often required to facilitate conductivity; thus the operating temperatures are limited to below the evaporation temperature of the solvent. In such membranes, water may be used as a vehicle mechanism for proton transport, for example in the form of H₃O⁺, where the protonated molecule diffuses through the material. In other materials, such as Nafion, water is required to dissociate the acid sites of a polymer backbone to promote hydrogen bonding necessary for proton mobility. At high water content, this class of materials exhibits extremely rapid proton conductivities, up to 10⁻¹ S/m², nearly the equivalent to 1M HCl. However, the low operating temperature requirements greatly reduce the catalytic activity on the device’s electrodes, which decreases operating efficiency and increases the amount of expensive precious metal catalyst needed.

On the other hand, ceramic electrolyte materials must operate at high temperatures to overcome the activation barrier of proton hopping through the crystalline lattice. These temperatures afford rapid catalytic activity on the two electrodes, increasing chemical reaction
kinetics, but the proton conductivities exhibited by these solid ceramic materials are far below those of their liquid and polymer-based counterparts, ranging from about $10^{-5}$ to $10^{-2}$ S/m.$^{22,24}$ The most common method for proton transport within ceramic materials is via the Grotthuss mechanism, whereby the proton hops through the lattice by the formation and cleavage of covalent bonds.$^{32-34}$ This proton transport process is also frequently observed in hydrogen-bonded networks, such as water, where the proton temporarily protonates a water molecule to form $\text{H}_3\text{O}^+$ before jumping to another water molecule.$^{35,36}$ The Grotthuss mechanism requires a minimum distance between the initial proton position and final destination in order to achieve a sufficient probability for a successful transfer. While the reorganization of water molecules requires very little energy input into the system, the reconfiguration of a crystalline lattice often requires a large amount of energy, $>48$ kJ/mol ($>0.5$ eV), in order to facilitate proton transport within the material.$^9,^{31,37}$ This leads to high activation energies for proton mobility within ceramics, thus requiring a high operating temperature for significant proton conduction to occur.

While high operating temperatures offer the benefit of rapid reaction kinetics, the harsh environment often leads to the sintering of catalyst particles on the electrodes, which are still necessary in high temperature devices, although in lower quantities. This sintering process reduces the surface area on which the reactions take place and degrades the catalyst performance.$^{38}$ Current research is thus exploring intermediate temperature (200-400°C) proton conducting materials that may offer high enough temperatures to facilitate reaction kinetics but low enough temperatures to inhibit catalyst sintering. Two techniques are presently being pursued to fill this “temperature gap”: 1) increasing the operating temperatures of traditional polymer electrolytes and 2) decreasing the temperatures required for ceramic proton conductors. While both of these avenues have led to the development of novel proton conducting materials,
perovskite type oxides have garnered much focus due to their high proton conductivities and the ability to manipulate numerous material properties through dopant substitution.

1.3 Perovskite Oxide Materials

First discovered by Gustav Rose in 1839, perovskites are ceramic materials composed of the general chemical formula ABX$_3$, where A and B are metal cations and X is a non-metallic anion (typically oxygen). While these materials can form a range of elaborate crystal structures, the simplest is the cubic perovskite structure, whereby the B-cation exhibits 6-fold coordination, surrounded by an octahedron of oxygen anions, and the A-cation forms a 12-fold oxygen coordinated complex. This basic structure, visualized in Figure 1.2, commonly becomes stretched or tilted to form orthogonal or tetragonal perovskite structures, respectively, due to differences in the ionic radii between the A and B cations. While this size mismatch causes crystalline distortion and a reduction of symmetry, it can also impart unique properties to the given perovskite. For example, within BaTiO$_3$ the undersized Ti atom may shift off-center within its oxygen octahedron and result in an electric dipole moment within the material, which imparts the property of ferroelectricity to the perovskite.

In the early 1980’s, Iwahara first demonstrated significant proton conduction capabilities within a number of II-IV perovskites, where the A cation consists of an alkaline earth metal and the B cation resides in Group 4 of the periodic table. These results were quickly followed by similar discoveries for I-V perovskites, as well as more complex perovskite materials. Proton conduction within perovskites begins with the ability to incorporate protons into the crystalline lattice. Protons can dissolve into the materials from water vapor or hydrogen gas, but solubility within traditional perovskites is often limited due to the unfavorable introduction of charged
defects into the electroneutral material.$^{30,49}$ To overcome this solubility limitation perovskites are almost always doped with acceptor ions to facilitate charge compensation within the oxide.$^{30,31}$ For example, a trivalent cation may be substituted for a tetravalent cation within a II-IV perovskite, such as BaCeO$_3$.$^{50,51}$ For every two trivalent cations incorporated into the lattice, one oxygen vacancy forms in order to maintain overall electroneutrality. Protons may then be dissolved into the material through the dissociative absorption of water vapor, where the hydroxyl ion fills an oxygen vacancy and the remaining proton forms a covalent bond with another oxygen within the lattice. This two-step “doping” and “hydration” process is essential to imparting proton conduction capabilities to perovskite oxide materials.$^{31,52}$

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**Figure 1.2 Perovskite Crystal Structure.** a) Unit cell of a cubic perovskite structure composed of divalent cations (green), tetravalent cations (cream), and divalent anions (red)  
 b) Expanded perovskite crystal structure.
Once protons are incorporated into the perovskite lattice, they may move within the materials via two different mechanisms: rotational diffusion and proton transfer. Numerous experimental and computational studies have examined these processes and have found that rotational diffusion around a single oxygen anion occurs rapidly and requires low-activation energies, <10 kJ/mol (<0.1 eV). On the other hand, proton transfer between neighboring oxygen ions often requires a temporary restructuring of the perovskite lattice and thus exhibits higher activation barriers. During this process, discussed previously as the Grotthus mechanism, the protons form a weak hydrogen bond with a nearest-neighbor oxygen ion. The O-H--O separation distance is reduced to about 2.8 Å as a result of the hydrogen bond, and the proton is able to jump to the secondary oxygen ion. This process requires an activation energy on the order of 39-58 kJ/mol (0.4-0.6 eV) and therefore requires high temperatures (> 800°C) for a significant number of transfer events to occur.

Below, we discuss more thoroughly the properties that influence both material hydration and proton mobility within perovskite oxides.

### 1.3.1 Hydration of Acceptor-Doped Perovskites

Material hydration occurs within perovskites through the dissociative absorption of water vapor. In the Kröger-Vink notation, this reaction is given as:

\[
\text{H}_2\text{O}(g) + \text{O}_\text{O}^X + V_\text{O}^- \leftrightarrow 2\text{OH}_\text{O}^- \quad (1.1)
\]

The oxide ion vacancies (\(v_\text{O}^-\)) and protonic defects (\(\text{OH}_\text{O}^-\)) are thus in equilibrium with each other. Assuming ideal behavior of all the species involved, this equilibrium condition can be described as:

\[
K = \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-\Delta H}{RT}\right) = \frac{[\text{OH}_\text{O}^-]^2}{[v_\text{O}^-][\text{O}_\text{O}^X][\text{H}_2\text{O}]} \quad (1.2)
\]
where the partial pressure of water is given in bars. Two important conditions must be met for Equation 1.2 to hold true. First, the conventional oxygen site restriction must be maintained, whereby the number of oxygen sites per formula unit is restricted to three:

\[
\left[ O_0^{X} \right] + [v^-] + [OH_o] = 3
\]  \hspace{1cm} (1.3)

Furthermore, the material must maintain overall electroneutrality, such that:

\[
2[v^-] + [OH_o] + [R_A] - [R_B'] = 0
\]  \hspace{1cm} (1.4)

where \( R_A \) constitutes an dopant substitution on the A site and \( R_B' \) denotes an dopant substitution on the B site.\(^{31,61,62}\)

Equation 1.2 reveals two important insights into perovskite hydration. First, the protonic defect concentration within a given perovskite can be manipulated through environmental conditions, such as increasing the partial pressure of water vapor or decreasing the temperature of the environment. Second, the thermodynamic parameters of the hydration reaction influence the ratio of oxygen vacancies to protonic defects. To maximize proton concentration within the perovskite, hydration enthalpy should be minimized and hydration entropy should be maximized.

To study the hydration thermodynamics of perovskites, researchers commonly utilize thermogravimetric analysis (TGA) to evaluate how proton concentration changes with environmental conditions. Using TGA the thermodynamic parameters of hydration can be calculated for various perovskites from Equation 1.2 by measuring how material weight, which correlates to the incorporation of protonic defects within the perovskite, varies with temperature and water partial pressure. Numerous TGA experiments,\(^{52,62,63}\) as well as alternative IR spectroscopy\(^ {52,64}\) and conductivity studies\(^ {65,66}\), have revealed several important parameters that
influence hydration thermodynamics within perovskite materials: the chemical composition and structure of the lattice and the choice of acceptor dopant.

Hydration enthalpy ($\Delta H$), or the energetic favorability of the material to absorb water, varies drastically between perovskites of differing compositions. Some perovskites, such as LaGaO$_3$, are rarely observed to incorporate protons into the material, even displaying endothermic hydration enthalpies.$^{67}$ Other perovskites, such as BaCeO$_3$, exhibit highly negative hydration enthalpies, as low as -150 kJ/mol (-1.6 eV).$^{48}$ Much research has focused on understanding how perovskite’s chemical and physical properties influence the material’s ability to readily hydrate. Norby et al. noted that the difference in electronegativities between the A and B cations, $\Delta X_{B-A}$, correlated well with the hydration enthalpy of the material. Figure 1.3 depicts a linear trend between $\Delta X_{B-A}$ and $\Delta H$, which can be fitted as:

$$\Delta H \text{ (kJ mol}^{-1}\text{)} = 400 \Delta X_{B-A} - 180$$

where Allred-Rochow electronegativities are used to calculate $\Delta X_{B-A}$. $^{30}$ This plot reveals that perovskites consisting of A and B cations with similar electronegativities exhibit more negative, or more thermodynamically favorable, hydration enthalpies. Additionally, Kreuer has observed that the basicity of the perovskite directly influences its ability to uptake water. He found that hydration enthalpy of perovskite-type oxides become more negative with the increasing basicity of the B-site element in the order: titanates $>$ niobates $>$ zirconates $>$ stannates $>$ cerates (i.e. cerates are the most basic and exhibit the most negative hydration enthalpies). $^{52}$ Unfortunately, it is not possible to quantitatively assess the basicity of ternary oxides, so we must rely on the electronegativities of constituent ions to try to understand how chemical properties of these perovskite oxides contribute to their hydration enthalpies.$^{30}$
Figure 1.3 Hydration enthalpy vs. electronegativity of constituent ions. This figure, taken from Norby et. al., demonstrates that hydration enthalpy increases, or becomes less favorable, as the difference in electronegativities between the A and B constituent ions within a perovskite oxide increases.

The perovskite’s physical structure also impacts the energetic favorability of material hydration. Although no correlation has been found between hydration enthalpy and the size of the perovskite lattice parameter, Munch et. al. observed that deviation from the ideal cubic perovskite crystalline structure decreases the extent of hydration within the material. The group compared hydration between perovskites with different levels of lattice symmetry: BaCeO$_3$ and SrCeO$_3$. While BaCeO$_3$ is composed of a wide lattice with little crystalline distortion, the small radius of Sr$^{2+}$ ions within SrCeO$_3$ causes significant tilting of the CeO$_6$ octahedrons. This deviation from the symmetric cubic perovskite structure leads to the formation of two different oxygen sites with disparate affinities for hydration. The differing interactions between the two oxygen sites with the surrounding cations alter the electron densities (basicity) of the oxygen ions, changing the O-H binding energies. Munch observed that BaCeO$_3$ became fully hydrated at
lower temperatures, while the SrCeO$_3$ exhibited only limited hydration at equivalent temperatures. The group concluded that the different chemical configuration of the two oxygen sites within the distorted perovskite reduced the energetic favorability of proton formation within the perovskite material.$^{68}$

While hydration enthalpy greatly varies between different perovskites, hydration entropy ($\Delta S$) remains more consistent despite changes in material chemistry and structure. For most perovskites the standard entropy change, $\Delta S^0$, of hydration is calculated as about -120 J/mol-K (-1.2 x 10$^{-3}$ eV/mol), which is equivalent to one mole of water losing all of it’s entropy as it absorbs into the material.$^{48}$ This corresponds to the water molecules losing all degrees of freedom once dissolved into the perovskite lattice from their gaseous state. However, hydration entropy can vary slightly between disparate perovskites. For example, BaZrO$_3$ demonstrates less negative hydration entropies than similar perovskites. Kreuer attributes this trait to a high entropy of protonic defects within BaZrO$_3$ due to more effective local softening in the proton environment.$^{52}$

The incorporation of acceptor dopants into the perovskite significantly impacts the material’s ability to absorb water. In cubic perovskites, the saturation limit, $S_o$, of protons within the material approaches the dopant ion concentration.$^{52}$ In other words, increasing the amount of acceptor dopant ions within the crystalline lattice can increase proton concentration by introducing more oxygen vacancies into the material. However, this principle only holds true so long as the acceptor dopant substitutes into a B cation lattice site. At dopant concentrations higher than 25%, the dopant ion commonly substitutes for A-site cations, reducing the number of oxygen vacancies throughout the material and limiting the proton saturation limit.$^{31}$
Besides inducing the formation of oxygen vacancies into which dissociated water molecules reside, the dopant ions also influence the thermodynamics of material hydration by changing the chemical nature of their neighboring lattice oxygens. The dopant species and concentration may alter the electron density (basicity) of nearby oxygen atoms, allowing the protons to bond more or less strongly depending on the chemical properties of the dopant ion. Figure 1.4 depicts how hydration enthalpy and entropy of BaCeO$_3$ become significantly more negative with the increase of yttrium dopant concentration. Kreuer suggests this phenomenon occurs because yttrium increases the basicity of the oxygen ions throughout the BaCeO$_3$ lattice, thus stabilizing the protons and increasing the energetic favorability of material hydration.$^{63}$

![Figure 1.4](image.png)

**Figure 1.4 Relationship between dopant concentration and hydration thermodynamic properties.** Figure, taken from Kreuer et. al.,$^{63}$ shows that hydration enthalpy and entropy decreases with increasing dopant concentration in yttrium doped barium cerate.

Dopant ions can also lead to a reduction in local lattice symmetry, which, as stated previously, can alter the favorability of perovskite hydration. Kreuer et. al. observed a reduced proton saturation limit within BaZrO$_3$ when the perovskite was doped with indium rather than
scandium. The group noted that the lattice maintained its cubic crystal structure upon the introduction of Sc ions, while the incorporation of In altered the lattice symmetry from ideal cubic to tetragonal. They argued that the reduction in symmetry of In-doped BaZrO$_3$ led to a decrease in the favorability of material hydration. Thus, they found it advantageous to match the size of the acceptor dopant ion and the host cation to avoid lattice distortion and the resultant reduction in material hydration.$^{69}$

### 1.3.2 Proton Mobility within Acceptor-Doped Perovskites

While proton concentration plays an important role in determining proton conduction across the perovskite material, proton mobility is an equally important factor in influencing overall protonic flux. Upon its incorporation into the perovskite, a proton resides in the valence electron cloud of an oxygen ion, forming a hydroxide ion, OH$_\text{O}$.\textsuperscript{49} The proton may then migrate throughout the material in two ways, either by hopping freely between stationary oxygen ions (the “Grotthus mechanism”) or by migrating as a hydroxide assembly through the lattice (the “vehicle mechanism”).\textsuperscript{44} Dominant theory in early perovskite research attributed proton transport to the latter process, as the activation energy for proton hopping, about 39-58 kJ/mol (0.4-0.6 eV),\textsuperscript{52} was just slightly lower than that of the oxygen ion, approximately 63-82 kJ/mol (0.65-0.85 eV),\textsuperscript{70} within a given perovskite. However, a series of isotope experiments completed by Iwahara and later confirmed by Norby indicated that proton mobility predominantly occurs independently throughout the perovskite lattice, rather than via hydroxide transport.$^{49,71}$

It is now widely accepted that proton transport within perovskites occurs first by a reorientation of the hydroxide ion through the formation of a hydrogen bond with a neighboring oxygen ion, followed by a proton transfer step between the two oxygens. Numerous molecular
dynamic simulations\textsuperscript{56,57} and experimental\textsuperscript{54,55} studies have revealed that protons rotate very rapidly around the local oxide ion with little energetic barrier. During this process the proton can form a transient but very strong hydrogen bond with neighboring oxygen ions. Kreuer found evidence for such hydrogen bonding from the broadening and red shift of the OH-stretching region in the infrared spectra of hydrated perovskites.\textsuperscript{23} The formation of a hydrogen bond can induce a distortion of the perovskite lattice, such that the oxygen separation distance ($d_{OH-O}$) decreases to $<280$ pm.\textsuperscript{52,59,60} Proton transfer then takes place during this contracted transition state configuration. While this basic process of proton transport throughout perovskites may be straightforward, several physical and chemical properties of the perovskite can retard or enhance proton mobility within these materials.

One of the most important physical factors that influences the ease of proton hopping through the perovskite is the “softness” of the crystalline lattice. This parameter relates to the ability for the material to deform to facilitate proton migration. In a “hard” oxygen environment, the proton must provide nearly all the energy for proton transfer via thermal vibrations. However, in “softer” environments, the reduction in oxygen separation distances that occurs during O-O vibrations may allow the proton to migrate in its vibrational ground-state.\textsuperscript{72} Surprisingly, Kreuer discovered that activation energy for proton hopping decreases with increasing lattice constants, such that perovskites with larger structural oxygen separation distances often display more rapid proton transport. These wider structures, attributed to large A-site cations, provide more dynamic mobility of the oxygen sublattice, which enables the perovskite to temporarily reconfigure the local environment around an interstitial proton. Such perovskites, such as BaCeO$_3$, exhibit amongst the highest proton conductivities of perovskite oxides.\textsuperscript{30,59}
While the size of the perovskite’s lattice parameter influences proton mobility, the lattice symmetry also impacts the proton’s ability to hop through the material. As described previously, perovskites that deviate away from the traditional crystalline structure can develop different oxygen sites with varying electron densities. In an orthorhombic structure, such as SrCeO$_3$, the cubic oxygen site degenerates into two different oxygen sites with probabilities of 1/3 and 2/3 for proton bonding. Each type of oxygen has a distinctly different basicity, which alters the proton binding affinity for the given site. These differing binding affinities, as well as biased rotational diffusion in these environments, are hypothesized to increase the activation barrier for proton mobility throughout such distorted lattices.$^{52}$

Proton mobility is sensitive to not only the perovskite lattice structure, but also to the chemistry of its constituent ions. The charge of the B-site cation can greatly influence the directional orientation of the O-H…O bond that forms and can alter the favorability of intraoctahedral mobility. In perovskites with highly ionic B-O bonds, such as BaCeO$_3$, the B-cation takes on a highly positive charge. This charge acts to repel protons, which decreases the favorability of proton transfer to oxygens within the BO$_6$ octahedron. Alternatively, the Zr-O bond within BaZrO$_3$ forms a more covalent bond, such that the Zr does not take on a strongly positive charge. Thus, strong Zr/H repulsion does not take place within these materials, so protons can transfer more favorably to close neighboring oxygens within the ZrO$_6$ octahedron. Materials with lattice chemistries that facilitate intraoctahedral mobility often exhibit lower bulk activation energies for proton hopping because the protons require less energy to transfer between nearby oxygen atoms.$^{31,57,73}$

Furthermore, the chemical and structural perturbations of the perovskite lattice caused by the incorporation of acceptor dopants plays a critical role in proton mobility. A mismatch in the
ionic radii of the dopant and host cation can cause structural contraction or expansion in the local lattice environment. These lattice deformations reduce the local symmetry around the dopant ion and may cause decreased proton mobility throughout the distorted perovskite.\textsuperscript{67,74,75} For example, Iwahara et al. report that proton conduction through BaCeO\textsubscript{3} decreases as dopant radii increases. The group attributes this phenomenon to more severe lattice distortion from larger dopant ions, which acts as a barrier to proton mobility in the local dopant environment.\textsuperscript{31,76}

Additionally, when the dopant and host ion change the basicity of the nearby oxygen ions, the proton binding affinities can be altered, changing the activation barrier required for proton hopping. In some scenarios, the dopant ion can chemically “trap” the proton in the local environment by increasing the O-H bond strength in surrounding oxygen ions.\textsuperscript{54,77} For example, when the yttrium dopant concentration is increased within BaCeO\textsubscript{3}, proton mobility decreases and activation enthalpy increases. This phenomenon mostly likely occurs because the yttrium increases the basicity of the surrounding oxygen ions, which increases the O-H bond strength, thus increasing the energy required for proton transfer.\textsuperscript{52} Finding a dopant ion that minimizes lattice distortion and causes positive or neutral chemical changes in the surrounding oxygen sublattice is important to maximizing proton mobility throughout perovskite materials.

1.3.3 Stability of Acceptor-Doped Perovskites

While high proton concentration and low activation energy for proton hopping are desirable characteristics for an effective perovskite proton conductor, the materials must also exhibit thermodynamic stability at high temperature ranges. Unfortunately, thermal stability and high protonic conductivity appear to be mutually exclusive in traditional acceptor-doped perovskites.\textsuperscript{52} Highly basic perovskites, such as cerates, tend to exhibit favorable hydration
properties but decompose into carbonates and hydroxides in the presence of acidic gases such as CO$_2$ and SO$_2$.\textsuperscript{31,78} Conversely, titanates, which traditionally show low favorability of protonic incorporation, are most stable at high temperatures in various acidic environments.\textsuperscript{23} Of the conventional perovskites explored to date, BaZrO$_3$ shows the most promising combination of high proton conductivity (bulk conductivities exceed that of BaCeO$_3$) and high thermodynamic stability. In the presence of CO$_2$ partial pressures found in air (38 Pa), BaZrO$_3$ remains stable at temperatures higher than 300°C, which is slightly better than several titanates.\textsuperscript{31} While the favorable combination of these two properties make BaZrO$_3$ a highly pursued and studied material, the primary limitation of the perovskite is slow grain boundary conductivities that limit the overall proton conduction throughout this material.

1.4 Perovskite Interfaces

1.4.1 Grain Boundary Conductivity in Acceptor-Doped Perovskites

Perovskite ceramic membranes range in width of about 0.1-1 mm,\textsuperscript{31,79,80} while an individual grain of the material only spans about 0.1-10 µm.\textsuperscript{81-83} Therefore, protons must travel through the bulk perovskite material within individual grains as well as across the boundaries of neighboring grains in order to propagate through the membrane. The “brick layer” model, visualized in Figure 1.5, gives an idealized depiction of the structure of a polycrystalline electrolyte membrane.\textsuperscript{84} Recent studies have been able to elucidate the bulk and grain boundary conductivities within perovskites from impedance spectroscopy experiments and have discovered that in many perovskites low grain boundary conductivities greatly decrease the overall conduction capabilities of the materials.\textsuperscript{85-87} BaZrO$_3$, for example, exhibits bulk conductivities more than two orders of magnitude higher than conductivities found at the grain
boundaries. While BaZrO$_3$ perovskites have proven to have among the highest bulk conductivities and thermal stabilities of those perovskites studied, the low grain boundary conductivities limit the material’s overall proton conduction capabilities. Thus, much research has focused on elucidating the cause of and reducing the effects that lead to low grain boundary conduction.

Figure 1.5 “Brick Layer” model. Idealized model of grains within multicrystalline ceramic materials. In this simplified case, proton conduction may be increased by increasing grain diameter ($d$) and decreasing grain boundary thickness.

Early theories suggested that structural variations at the grain boundary impede the mobility of protons across the interfacial region. At the boundary between two perovskite grains, lattice distortion commonly occurs to minimize the interfacial energy. Researchers hypothesized that this deviation away from the bulk crystalline lattice may lead to an increase in the activation energy required for proton mobility in this region. More recent studies have led to an alternative theory, suggesting a space charge effect may be culpable for the reduced conduction capabilities across the perovskite grain boundary. In this model (Figure 1.6), researchers propose that the preferential segregation of charged defects, namely oxygen
vacancies, to the grain boundary induces a positively charged grain boundary core. The positive charge induces a gradient of charged defects in the regions adjacent to the grain boundary interface, such that positively charged defects like protons are repelled away from the grain boundary. This depletion region, known as the space charge layer, thus causes high resistance to proton mobility across the grain boundary region due to a reduction in proton concentration in the area.

Figure 1.6 Space charge layer. A space charge layer may develop at the grain boundary interface due to the formation of a grain boundary core charge. The grain boundary core can take on a charge based on defect segregation to the GB interface. The build up of a core charge can induce an electric field, which acts upon defects in the near GB region. If a positive grain boundary core charge develops, then the concentration of relatively negatively charged defects will increase relative to the bulk near the GB. Alternatively, the concentration of positively charged defects will decrease relative to the bulk in the near GB environment. The region where defect concentration is either enhanced or depleted is known as the space charge layer.

While both theories likely play a role in the reduction of proton mobility in the grain boundary region, most researchers now attribute the predominant origin of proton impedance across the interface to the space charge effect. Maier and his team provided one source of evidence supporting this theory when they switched the mobile charge carrier from protons to
electrons within a BaZrO$_3$ samples. In the presence of a positively charged grain boundary core, the concentration of negatively charged defects, such as electrons, is expected to increase, causing more rapid conduction of the defect in the area. However, electron concentration in traditional perovskite samples is too low to observe this effect on electrical conductivity. Upon introducing excess electrons into a highly reduced sample of BaZrO$_3$, the group observed that grain boundary resistance to electron conduction across the interface vanished and concluded the most likely cause for enhanced conduction was due to the presence of a positively charged grain boundary core.$^{92}$

Although numerous experimental results have provided indirect evidence that a positive grain boundary core charge is responsible for the low grain boundary conductivities in perovskites, the specific origin of the grain boundary core charge has still not been elucidated.$^{92-94}$ Thus, researchers have used both experimental and theoretical techniques in an attempt to discover the driving force of defect segregation that causes charge buildup at the grain boundary interface.

Nyman et. al. recently performed a density functional theory study to probe $V_O$ segregation at a tilt grain boundary of BaZrO$_3$ to identify the most stable configuration of the defect in the interfacial region. The results indicated an energetic driving force of about -120 kJ/mol (-1.25 eV) for oxygen vacancy segregation to the first subsurface layer of the crystal. The authors calculated that this favorable $V_O$ formation energy would give rise to an electrostatic potential barrier of 53 kJ/mol (0.55 eV), similar to those seen in experimental studies.$^{95}$ While the group suggests the origin for oxygen vacancy segregation to the first subsurface layer arises from an electrostatic repulsion of oxygen ions between the two crystalline surfaces, the authors give no evidence to substantiate this claim. The findings do support the hypothesis that
preferential segregation of oxygen vacancies may be the source of a positive grain boundary core, but the study also highlighted the need to clearly understand how and why $V_O$ segregation occurs in the grain boundary region. Only once this knowledge is developed will researchers begin to be able to more rationally design perovskites with reduced positive grain boundary core charges that will exhibit enhanced proton conduction across these regions.

Shirpour et. al. took a different approach to understanding defect segregation at the BaZrO$_3$ grain boundary by using a combination of transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDXS) to investigate dopant segregation at the perovskite interface. The authors suggested that the positive charge developed by oxygen vacancy segregation to the grain boundary could be offset by the transport of negatively charged dopant ions to the interfacial area. While negatively charged dopant ions are immobile at traditional operating temperatures (600-800°C), they are able to migrate under annealing temperatures (>1500°C), whereby they may segregate to the most energetically favorable state and are then fixed into place during normal operation. Shirpour doped BaZrO$_3$ with relatively large yttrium dopants and similarly sized scandium dopants compared to the Zr ions for which they were substituted. The segregation of the two different dopants were then compared to elucidate how size effects influence grain boundary segregation. The group hypothesized that oversized dopants that induce elastic strain in the local environment might preferentially segregate to the grain boundary region to alleviate the lattice distortion. However, the group saw no significant differences in grain boundary segregation between the two different dopant ions. They concluded that elastic energy does not constitute a major driving force for defect segregation. Rather, Shirpour suggested that dopant migration to the grain boundary region may result from an
electrostatic interaction between the positively-charged GB core and the relatively negatively-charged dopant ions.

While recent research has begun to pursue the origin of the grain boundary core charge that develops in perovskites, the complex electrostatic interactions that occur between the different charged defects at the material interface make it difficult to discern the driving force that dictates defect segregation. Understanding how lattice distortion, surface cleavage, and defect interactions (among other compounding factors) influences the grain boundary core and, subsequently, proton conduction through this region are critical toward designing new perovskites with improved conduction capabilities.

1.4.2. Perovskite-Vacuum Interfaces

One method of understanding the complex grain boundary environment is to begin by studying a simplified perovskite-vacuum interface. While this interface does not include electrostatic interactions between the crystals, the perovskite-vacuum interface may help isolate many of the complex elements to gain a more fundamental understanding of defect segregation and proton mobility. In order to study these factors in silico, the stability of various surface facets must be explored.

A cubic perovskite crystal may be cleaved along numerous crystalline facets. The (001) facet is the most closely packed facet, with the (110) and (111) facets following. Along each one of these facets, the crystal can be cleaved to reveal two complementary surfaces. Since perovskites are an ionic material, the charge of each layer must be considered in determining the stability of each of these surfaces. Classical electrostatic criteria dictate that the stability of a surface depends on the charge distribution of the layers that repeat perpendicular to the surface.
When the repeating unit has a dipole moment $\mu=0$, the surface is potentially stable. However, when the repeating layers form a non-zero dipole moment, the polar surface has a diverging electrostatic surface energy rendering the surface unstable.\textsuperscript{97,98}

For BaCeO$_3$, along with other II-IV perovskites, cleavage along the (001) facet results in the formation of non-charged layers, specifically BaO and CeO$_2$, which each sum to a net neutral charge. However, the (110) and (111) surfaces form individual layers that sum to a non-neutral charge. The BaCeO and O$_2$ surfaces of the (110) facets result in +4 and -4 net charges, respectively, while the BaO$_3$ and Ce layers perpendicular to the (111) facet form -4 and +4 charged layers, respectively. These charged layers induce a dipole moment between the repeating units equal to $\mu=\sigma R_1$, where $\sigma$ is equal to the absolute value of the charge density of each layer and $R_1$ is the distance between the layers within a repeating unit. The total dipole moment across the slab $M=N \sigma R_1$ is proportional to slab thickness. In large slabs, when the number of layers $N \rightarrow \infty$, the electrostatic contribution to the surface energy diverges and the surface becomes unstable.\textsuperscript{97}

While ideal polar surfaces are classically considered unstable, there are modifications that can be made to the outer surface layers that act to cancel surface polarity and increase surface stability. One such method acts to cancel out the macroscopic component of the dipole moment through a restructuring of the surface. Here the surface is reconfigured through the deletion or addition of atoms such that the outer layer takes on a charge density:

$$\sigma' = \frac{\sigma R_2}{R_1+R_2}$$

where $R_2$ is the distance between repeating units. The total dipole moment is now no longer proportional to slab thickness, such that $M = \sigma R_1 R_2/(R_1+R_2)$.\textsuperscript{97,98} The surface can thus be stabilized if the charge compensation criterion from Equation 1.6 is met. In the (110) and (111)
facets of BaCeO$_3$, where repeating layers take on a ±4 charge and R1~R2, the surface may become more stable by reconfiguring each surface such that the outer layer retains a ±2 charge. For example, the BaCeO (110) surface takes on a +4 charge. The charge compensation criteria can be met through atomic deletion by forming either Ba- or CeO-surface, each with a net charge of +2. While these non-stoichiometric surfaces may show enhanced surface stability compared to their stoichiometric counterparts, stoichiometric surfaces can undergo enhanced stabilization through electron redistribution in response to the electrostatic field. Whether a polar surface undergoes structural reconfiguration or electron redistribution as a means of surface stabilization depends primarily on energy considerations.$^{97}$

Several density functional theory studies have probed the stability of numerous perovskite surfaces.$^{99-103}$ One of the most common assessments of surface stability is the energy required to cleave a crystal, known as the cleavage energy. In perovskites, the average cleavage energy for a given surface facet may be calculated from the two complementary surfaces:

$$E_{cl} = \frac{1}{4} [E_{slab} (A) + E_{slab} (B) + \frac{n}{m} E_{bulk}]$$ (1.7)

where $E_{slab}$ equals the energy of the unrelaxed symmetric slab of termination A or B, $E_{bulk}$ represents the energy of the bulk unit cell, $n$ denotes the total number of chemical formula units in the A- and B- terminated slabs combined, and $m$ signifies the number of chemical formula units in the bulk supercell. Furthermore, the stability of the complementary surfaces, A and B, can be distinguished from each by allowing the surfaces to relax symmetrically on both sides of the cell and calculating the relaxation energy:

$$E_{relax} (A) = \frac{1}{2} [E_{slab}^{relax} (A) - E_{slab}^{fixed} (A)]$$ (1.8)

This surface stability assessment has been completed for numerous perovskites, including BaZrO$_3$,$^{99}$ BaCeO$_3$,$^{100}$ BaTiO$_3$,$^{101}$ PbTiO$_3$,$^{102}$ and CaTiO$_3$,$^{103}$ to identify the most stable
perovskite surface. While the close-packed (001) surface is commonly found to the most stable perovskite surface, a comparison between stoichiometric and non-stoichiometric polar (110) and (111) surfaces revealed that the restructured surfaces most often had the lower cleavage energies. This finding provides evidence that the reconfiguration of the polar surfaces of perovskite oxides is a more adequate form of polarity compensation than a redistribution of electrons in the stoichiometric terminations.

1.4.3 Perovskite Catalysts

While studying the perovskite-vacuum interface may yield a more fundamental understanding of proton and defect chemistry in the complex GB environment, it can also be used to probe catalytic properties of perovskite surfaces. Attention has long been focused on the promising conduction capabilities of perovskite oxides; yet studies of the material have broadened to explore the viability of perovskites as catalysts within electrochemical devices. Recent computational and experimental studies of the oxygen reduction reaction (ORR) on Pt-based catalysts have revealed that the d-band center of the Pt metal acts as a descriptor for catalyst activity in acidic environments (O$_2$ + 4H$^+$ + 4e$^-$ $\rightarrow$ 2H$_2$O).$^{104,105}$ Screening for metal surfaces in which the optimal d-band center is achieved has identified promising new Pt-based catalysts for the ORR.$^{106,107}$ Within the basic environment of alkaline fuel cells and metal-air batteries, transition metal oxides have shown reasonably high activity for the ORR (O$_2$ + H$_2$O + 4e$^-$ $\rightarrow$ 4OH$^-$). However, the reaction mechanism of the ORR is not well understood on the complex surfaces of metal oxides, such as perovskites, making it difficult to screen for new materials with enhanced catalytic activity.$^{108,109}$
Despite not fully understanding the ORR reaction mechanism on perovskite surfaces, several recent studies have attempted to identify material properties (descriptors) that influence catalyst activity. Suntivich et. al. used a thin film rotating disc electrode to compare ORR activity on a number of lanthium-based perovskite catalysts. The group identified an optimal filling of the $\sigma^*$-antibonding orbital in the surface transition metal ions that maximizes ORR activity. Additionally, Lee et. al. probed how the electronic properties of oxygens within the bulk material, an area much easier to study \textit{in silico}, impacts the surface activity for the ORR. Here the group discovered that the bulk oxygen p-band center correlates well with catalytic activity of the perovskites studied. These recent findings motivate further investigation of material and surface properties that may inform catalyst design. Particularly, understanding proton adsorption on perovskite surfaces may yield insights into how to enhance the ORR on perovskite catalysts in acidic environments ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$), which would help reduce the reliance on expensive precious metal catalysts.

1.4.4 Perovskite-Metal Interface

Despite interest in replacing precious metal catalysts with perovskite materials, traditional electrochemical devices, such as solid oxide fuel cells (SOFCs), rely on these metals for sufficient performance. The incorporation of the metal electrode causes the formation of three phase interfacial regions between the electrode, electrolyte, and the gaseous reactants, known as the triple phase boundary (TPB). In SOFCs with proton conducting electrolytes, such as perovskites like BaZrO$_3$, protons generated at the anode travel through the electrolyte and contribute to the formation of water on the cathode electrode. Thus, incorporation of protons from triple-phase boundary sites into the bulk of the electrolyte material is an important and
potentially rate-limiting step that plays a critical role in fuel cell performance, yet little is currently known how proton stability varies at within this heterointerfacial region.

The complexity of the heterointerface makes it difficult to probe proton behavior near the TPB interface, yet there is a general understanding of how proton concentration is altered in the interfacial environment of oxides upon the addition of a metal heterointerface. When a metal and an oxide with dissimilar work functions are combined to form a heterojunction, a band bending effect takes place to equalize the Fermi level at the interfacial region. If the metal has a greater work function than the oxide material, the perovskite in this case, then electrons from the oxide spill into the upper energy levels of the metal, leaving behind an increased concentration of electron holes. Since holes and protons are in equilibrium with each other, this leads to an enhanced concentration of protons in the perovskite near the heterointerface compared to the density of protons in the perovskite bulk. This region with higher proton concentration is considered a space charge layer.

![Figure 1.7 Space charge layer at a semiconductor-metal heterointerface.](image)

A fundamental study of proton chemistry at the heterointerface may yield not only important insight into proton stability near the TPB, but it may also reveal a method of
enhancing proton conduction within the perovskite material. Recent work in the O’Hayre group has shown that the incorporation of metal nanoparticles into yttrium-doped barium zirconate led to the enhancement of proton conductivity within the membrane. Tong et. al. found that the Pd nanoparticles tended to cluster along the grain boundaries of the ceramic material and caused an increase in both GB and overall conductivity. Samples with the metal particles showed a 1.5-2.7 times increase in conductivity compared to the pure control. The group hypothesized that a band bending effect at the heterointerface due to the addition of Pd nanoparticles into the BZY lattice led to an increase in proton conduction throughout the perovskite ceramic.\(^{117}\)

1.5 Summary

Perovskite oxides exhibit promising attributes for both proton conduction and catalytic applications within electrochemical devices. However, these complex materials contain numerous local environments in which proton stability and defect chemistry can greatly influence the processes for which these perovskites are being implemented. This thesis will focus using first principle techniques to examine proton stability in a range of perovskite environments, including the material bulk, surface, and heterointerface. The goal of this work is to gain a stronger understanding of proton chemistry within perovskite oxides as well as to develop novel strategies to investigate and screen for perovskites with enhanced material properties.

1.6 References


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CHAPTER II

THESIS OBJECTIVES

2.1 Overview

The goal of this work is to use first principle computational techniques to gain a fundamental understanding of proton and defect chemistry within perovskite oxides in order to identify strategies to increase proton concentration and improve overall proton conductivity within these materials. Proton stability fluctuates within different environments of the complex perovskite membrane. In the material bulk, proton concentration is limited by material hydration restrictions that are dictated by lattice composition and geometry.\(^1,2\) Here, hydration refers to the process by which protons are incorporated into the perovskite via the dissociative absorption of water vapor.\(^3,4\) Once introduced into the material, protons tend to segregate away from the grain boundaries on account of a positive core charge that develops at the material interface.\(^5-7\) This decrease in proton concentration at the grain interface limits proton conduction between perovskite grains. Additionally, proton stability at the perovskite surface and the triple phase boundary within electrochemical devices influences the binding strength of protons on the surface and the mobility of protons into and out of these proton conducting membranes, affecting catalytic properties and impacting the overall performance of the electrochemical devices.\(^8-10\)
This project aims to use *ab initio* techniques to assess proton and defect chemistry in the perovskite bulk and grain boundary regions and to explore proton stability at the perovskite-vacuum surface and perovskite-metal heterointerface. Barium cerate (BaCeO$_3$) and barium zirconate (BaZrO$_3$) will serve as model perovskite compounds to complete these studies. *The specific goals of this project are to understand the thermodynamic driving forces of material hydration in the bulk, to examine the origin of the unfavorable interfacial charge at the grain boundary interface, and to investigate how proton stability changes in both the simplified perovskite-vacuum and complex perovskite-metal interfacial environments.*

The specific aims of this thesis are:

1. **Develop a method to predict hydration in bulk perovskite materials by using first principle techniques to study hydration thermodynamics.**
2. **Investigate defect segregation at the perovskite surface to determine how the grain boundary core charge may be mitigated.**
3. **Examine proton adsorption energies at the perovskite-vacuum and perovskite-metal interfaces to identify how the introduction of metal atoms influences proton stability.**

### 2.2 Thesis Organization

Below is a brief description of the contents in the remaining chapters of this thesis.

**Chapter 3. Methods**

Chapter 3 provides an overview of Density Functional Theory (DFT), the primary technique used toward the completion of this thesis, and outlines the computational assumptions and limitations of this method.
Chapter 4. A theoretical study of the influence of dopant concentration on the hydration properties of yttrium-doped barium cerate

A model using in silico and a priori techniques is developed to explore the thermodynamic tradeoff between hydration enthalpy and entropy as a function of dopant concentration and temperature within yttrium-doped barium cerate (BCY).

Chapter 5. First-principles study of the stability of orthorhombic BaCeO3 surfaces

The stability of the (001), (110), and (111) surfaces of BaCeO3 is assessed by computing cleavage and relaxation energies for a number of surface terminations. Additionally, alternative DFT methodologies and slab configurations are probed to identify the most stable BaCeO3 system for subsequent surface studies.

Chapter 6. Computational investigation of defect segregation at the (001) surface of BaCeO3 and BaZrO3: the role of metal-oxygen bond strength in controlling vacancy segregation

DFT is used to probe the segregation of yttrium dopants and oxygen vacancies in the near surface environment of BaCeO3 and BaZrO3 (001) surfaces. Based on the results, a suggestion to mitigate the development of a positively charged grain boundary core is provided.

Chapter 7. An ab-initio investigation of proton stability at BaZrO3 interfaces

Proton stability is probed near both the perovskite-vacuum and perovskite-metal interfaces to model several environments found within the complex perovskite membrane. An electronic analysis of the oxygen atoms within the homogeneous perovskite systems reveals an important descriptor of proton adsorption energy that can be used to screen for perovskites with enhanced conduction capabilities.
Chapter 8. Conclusions and Future Directions

The work in the previous chapters is summarized and the main results are reviewed. Recommendations for future work to build upon this thesis are included.

2.3 References


CHAPTER III

COMPUTATIONAL METHODS

3.1 Density Functional Theory

The progress made toward computational speed and efficiency has enabled theoretical scientists to probe more complex and elaborate systems using *ab-initio* (from first principles) quantum chemistry techniques. This avenue of study allows researchers to probe material properties on an atomistic level and facilitates the calculation of material energy, geometrically optimized structures, and reaction energies. The basis of quantum chemistry is the Schrödinger Equation, which describes the quantum state of a physical system via the time independent equation:

\[ \hat{H} \psi = E \psi \quad (3.1) \]

In this equation, \( \hat{H} \) is the Hamiltonian operator and \( \psi \) represents the eigenstates, or the set of solutions to the Hamiltonian. In the Schrödinger equation, each solution, \( \psi_n \), has an associated eigenvalue, \( E_n \), which satisfies the eigenequation. The Hamiltonian corresponds to the energy of a given system and takes on the general form:

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U \quad (3.2) \]
where the first term, $\frac{\hbar}{2m} \nabla^2$, describes the kinetic energy of the system and the second term, $U$, describes the potential energy.

In systems with more than one electron, the Hamiltonian becomes more complex due to the incorporation of further interaction terms. The complete Schrödinger equation for a multi-electron system (also known as the Hartree-Fock equation) becomes:

$$\left[ \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i<j}^{N} U(r_i, r_j) \right] \psi = E\psi$$  \hspace{1cm} (3.3)

where the first term describes the kinetic energy of each electron, the second term defines the interaction of each electron with the atomic nucleus ($V$), and the third term dictates the interaction energy between different electrons ($U$). Within the equation, $m$ is given as the mass of an electron and $E$ is the ground state energy of the electrons. The equation is a function of the spatial coordinates of each of the $N$ electrons of the system.

The Schrödinger equation cannot be solved analytically for a system comprised of more than a single hydrogen atom due to the complex electron-electron interactions.$^3$ Thus, Hohenberg and Kohn developed an alternative method to solve the Schrödinger equation for a multi-body system. Ultimately, the pair proved two mathematical theorems that provide the foundation upon which the field of Density Functional Theory was developed.$^{4,5}$ The first theorem states, “The ground state energy from Schrödinger’s equation is a unique functional of the electron density that depends on only 3 spatial coordinates.” This allows the 3-dimensional coordinates of all electrons in the system to be replaced by the density of electrons at a particular position in space, $n(r)$. This reduces the number of independent variables of the full wave function from $3N$ coordinates to just 3 coordinates. The ground state energy can therefore be given as a functional of the electron density, $n(r),$ such that:

$$E[n] = T[n] + E^{\text{coulombic}}[n] + E^{\text{XC}}[n]$$ \hspace{1cm} (3.4)
where $T$ is the kinetic energy, $E_{\text{coulombic}}$ is the potential energy due to electron-electron and electron-nuclear interactions, and $E_{\text{XC}}$ is the exchange-correlation energy (described in more detail below).

Hohenberg and Kohn’s second theorem states, “The density that minimizes the total energy is the electron density that corresponds to the solution of the Schrödinger Equation.” Kohn-Sham proved that the electron density could be solved using a set of equations that describe each of the electrons as non-interacting particles. The Kohn-Sham (K-S) equation for a single electron is given as:

$$
\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r) + V_h(r) + V_{XC}(r)\right] \psi_i(r) = E_i \psi_i(r) \quad (3.5)
$$

While the K-S equation resembles the Hartree-Fock equation (3.3), the difference lies in the lack of summation over all electrons in the system. Instead, the K-S equation (3.5) represents a single electron wave function that depends only on three spatial variables, $\psi_i(r)$. $V(r)$ describes the interaction between the electron and the collection of atomic nuclei. The Hartree potential, $V_h(r)$, represents the Coulombic repulsion between the electron described by the given K-S equation and all the electrons in the system. Electron exchange and correlation effects are included in the $V_{XC}(r)$ term in equation 3.5; expressing $V_{XC}(r)$ in terms electron density allows DFT to treat systems with multiple atoms much more efficiently than methods that achieve comparable accuracy.\(^6\)

The calculation of the exchange and correlation terms is a source of error within DFT. The only case where this functional can be described exactly is for a uniform electron gas. In the local density approximation (LDA),\(^6\) the $V_{XC}$ is defined by setting the term to the known exchange-correlation potential of a uniform electron gas at the electron density for a given spatial position:
\( V_{xc}(r) = V_{xc}^{\text{electron, gas}}[n(r)] \)  

(3.6)

This method has been widely replaced by the generalized gradient approximation (GGA),\(^7\) which accounts for both the local electron density as well as the charge gradient of the electron density. To describe the gradient of the electron density, several GGA functionals have been developed, including the common Perdew Wang 91 (PW91)\(^7\) and the Perdew-Burke-Ernzerhof (PBE)\(^8\)/revised PBE functionals.\(^9\) The PW91 functional was used for the work completed in this thesis because it has been shown to be the benchmark for accurately describing both slabs and solid materials.

DFT uses the self-consistent field (SCF) method to solve the K-S equation for a given system.\(^4\) The following algorithm outlines this technique:

1. A trial electron density is defined from initial inputs.
2. The trial electron density is used to solve the K-S equation to find a single particle wave function, \( \psi_i(r) \).
3. The electron density is recalculated from \( \psi_i(r) \), dictated by:
   \[
   n(r) = 2 \Sigma_i |\psi_i^*(r)\psi_i(r)| \tag{3.7}
   \]
   where \( |\psi_i^*(r)\psi_i(r)| \) is the probability that an electron in the wave function \( \psi_i(r) \) is located at position \( r \).
4. The electron density is used to compute the total energy. This energy is then compared to the total energy of the previous cycle. If two successive iterations yield energies within a given tolerance, then the final \( n(r) \) is defined as the ground state electron density and is used to compute the energy of the system. If the two energies don’t pass the tolerance criteria, then the process must be repeated using the final \( n(r) \) as the initial electron density.
DFT calculations in this thesis were completed using the Vienna Ab-Initio Simulation Package.\textsuperscript{10}

\subsection*{3.2 Basis Sets in DFT}

A basis set is a set of functions that, when combined in linear combination, create molecular orbitals. In DFT these functionals are used to describe the Kohn-Sham molecular orbitals. Different types of basis sets are used depending on the type of model being studied.\textsuperscript{1} Since this thesis attempts to model large systems representing different perovskite materials, compared to single small molecules, the system cannot be modeled in its entirety. There are two main approaches to modeling large systems such as these. A finite cluster model truncates the larger system by incorporating only a finite number of atoms in the model. Such methods are known to be susceptible to error at the cluster edge. These models use localized functions, such as Gaussian type orbital (GTO) or Slater type orbital (STO) basis sets, that are radially and angularly dependent on the electron distribution.\textsuperscript{3} Molecular orbitals can be formed through the linear combination of atomic orbitals (LCAO) described by the basis set:

\begin{equation}
\psi = \sum_n c_n \phi_n \tag{3.8}
\end{equation}

The coefficient $c$ weights the combination of the atomic orbitals, $\phi_n$. To minimize the energy of a molecule, the coefficients of the linear combination must be optimized using the self-consistent field procedure described above.

An alternative to the cluster model is the periodic system that uses plane waves to employ periodic boundary conditions.\textsuperscript{11} In this manner, the unit cell is replicated in all dimensions semi-infinitely and edge effects are absent. The plane waves describe the Kohn-Sham orbitals, such that

\begin{equation}
\psi_k(r) = e^{ik\cdot r} f_i(r) \tag{3.9}
\end{equation}
where \( f_i(r) \) is the function of the reciprocal lattice vectors of the unit cell. The wave vectors, \( k \), comprise the Brillouin zone in the reciprocal space and are defined by the boundaries of \(-\pi/a < k < \pi/a\), where \( a \) is the length of the unit cell. While the true k-point density of a material’s unit cell is quite large, only a few k-points are often needed to accurately represent the Brillouin zone. The Monkhorst-Pack method has been utilized for all k-point sampling in this thesis.\(^{12}\) Furthermore, k-point point sampling for bulk material calculations were completed by sampling in all Cartesian directions, while the k-points were only sampled across the plane formed by the surface for interfacial calculations.

A complete expansion of the plane wave basis set to achieve perfect accuracy is not computationally possible. Therefore, the plane waves must be truncated to reduce the basis set to a finite size. This point is dictated by the cut-off energy, which means that only vectors whose kinetic energies are lower than the pre-defined cut-off energy will be included in the expansion of the basis set. The cut-off energy presents a tradeoff between computational accuracy and resources. For example, higher cut-off energies yield more accurate results, but require more computational resources. Therefore, for this thesis, the cut-off energy for each study was determined from a series of convergence tests to determine the minimum cut-off energy necessary to achieve suitably accurate results. The values of the cut-off energies for each study are described in detail in each of the subsequent research chapters.

Since atomic orbitals for larger atoms can be quite complex, plane wave basis sets often only describe the valence electrons of an atom, while an “effective core potential,” or pseudopotential, depict the electron core.\(^1\) These core electrons are typically located close to the nucleus, resulting in large wave functions and electron gradients near the atomic nuclei. The pseudopotential is comprised of an electron density that matches the important physical and
mathematical properties of the true electron core. At the interface between the valence and core electrons, the valence wavefunctions tend to have rapid oscillations because they must be orthogonal to the core states, which is computationally expensive to accurately model. The pseudopotential used in this thesis, the projector augmented wave (PAW) method, addresses this issue by converting the oscillations of the valence wavefunctions into smooth wavefunctions that are more computationally convenient.\(^\text{13}\)

### 3.3 Summary

Density functional theory allows researchers to gain a quantum level understanding of large, complex systems through the approximation of the Schrödinger equation. By replacing the 3-dimensional coordinates of all electrons in the systems with the density of electrons around each atom, the energy of the system, along with a variety of other material properties, can be calculated. In this thesis, DFT was primarily used to determine the geometrically optimized arrangement of atoms within the perovskite system, as well as the corresponding material energy of the fully optimized structure. Additionally, electronic properties, such as atomic charge and electronic structure, were probed to gain a more complete understanding of the trends and phenomena that were discovered. More thorough explanations of how these analyses were carried out within DFT are given in the corresponding research chapters.

### 3.4 References


4.1 Introduction

The advancement of highly efficient proton conducting materials is essential to the development of a variety of electrochemical devices, such as fuel cells, batteries, and hydrogen sensors.\(^1\)\(^2\) Current research is focused on creating solid oxide materials that exhibit high ionic conductivity while maintaining structural and chemical stability over a wide temperature range.\(^3\)

Within this class of materials, perovskite-type oxides display high proton conductivities and thus have garnered considerable attention for their application towards solid-state proton conductors.\(^4\) Acceptor-doped barium cerates (BaCeO\(_3\)) are often chosen as model compounds for perovskite-type oxides as they remain among the most efficient ion conducting materials in this class.\(^3\)\(^5\)

To achieve these unique ionic conducting properties, mobile protons are introduced into the perovskite material through a two-step process. First, oxygen vacancies are formed within the lattice by integrating an acceptor dopant, typically a trivalent cation, into the oxide, partially replacing tetravalent cation species. To maintain overall electroneutrality, one oxygen vacancy
forms for every two trivalent acceptor dopant ions incorporated into the matrix. The doped material is then exposed to a humid atmosphere where protonic defects are introduced into the lattice through the dissociative absorption of water vapor.\textsuperscript{3,4} In the Kroger-Vink notation, this reaction is given as:

\[
\text{H}_2\text{O} + \text{V}^{\prime\prime}_0 + \text{O}_0^X \leftrightarrow 2 \text{OH}^*_0
\] (4.1)

where V\textsuperscript{\prime\prime}_0 represents an oxygen vacancy, O\textsuperscript{X}_0 represents an oxygen present in the lattice, and OH\textsuperscript{*}_0 represents a protonic defect.

Infrared spectroscopy and diffraction experiments have investigated the structure of protonic defects in perovskite-type oxides as a result of material hydration. These studies have demonstrated that the protons bond with oxygen anions, while simultaneously forming weak hydrogen bonds with nearest-neighbor oxygen ions.\textsuperscript{6-8} This proton bonding structure has been confirmed through several quantum mechanical studies.\textsuperscript{9-11} Additionally, molecular dynamic simulations, coupled with experiments, have studied proton behavior in these materials and have concluded that proton diffusion occurs via the Grotthuss mechanism, in which a proton rapidly rotates around the bound oxygen species and then jumps to a neighboring oxide ion.\textsuperscript{4,6,12}

Such studies of the structure and behavior of protonic defects in perovskite-type oxides have led to a basic understanding of proton conduction within these materials.\textsuperscript{2} However, proton flux through the oxide is dependent on both the rate of proton hopping, which is dictated by the structure and behavior of protonic defects, and the concentration of charge carriers, which relies on the thermodynamics of hydration. Since the activation energy for proton hopping is already very low,\textsuperscript{13,14} one strategy towards improving proton conduction through perovskites is increasing the density of protonic defects through increased material hydration. In doped perovskite oxides, the dopant species and concentration greatly influence the extent of hydration.
Numerous thermal gravimetric analysis (TGA) experimental studies have shown that hydration enthalpy and entropy become more negative with increasing dopant concentration, but few quantum mechanical computational studies have probed the fundamentals of perovskite hydration.

One recent *ab initio* study has introduced a method that combines density functional theory (DFT) calculations and thermodynamic models to investigate protonic stability in barium zirconate. Since DFT calculations are a zero-temperature, zero-pressure technique, it can be difficult to directly compare data from high temperature experiments with computational results. Bjorketun et al. outline an approach to compensate for temperature and pressure conditions in their theoretical calculations. Using this technique they were able to calculate thermodynamic hydration values for doped BaZrO$_3$ that were comparable with experimental values. However, these results did not directly account for dopant-proton and dopant-oxygen vacancy interactions, thus the resultant hydration values were not dependent on dopant species or concentration.

Norby et al. recently published a series of studies that also used DFT simulations to calculate hydration enthalpy for several perovskite materials. Norby’s computational approach is simpler than Bjorketun’s intensive procedure because it does not correct for the zero-temperature, zero-pressure nature of DFT calculations. Although they did not compensate for these effects, Norby’s group was able to calculate hydration enthalpies that were comparable to experimental values for several perovskite oxides, including CaZrO$_3$, SrZrO$_3$, and BaZrO$_3$. However, only undoped materials were considered in these DFT studies, so the dependence of dopant concentration on hydration properties was not investigated.

This paper presents a quantum mechanical study of the effect of dopant concentration on several hydration properties of yttrium-doped barium cerate (BCY). BCY is a common reference
compound for perovskite-type materials because of its high proton conduction capabilities and the breadth of research and data available pertaining to hydration and defect equilibrium within the oxide.⁵ We first report the hydration expansions and enthalpies for several concentrations of yttrium-doped barium cerate. Studying the expansion properties of perovskites can help ensure that the materials do not crack or fail when exposed to water vapor, while understanding hydration enthalpy can shed light on important thermodynamic properties. Next, the hydration enthalpy trends are explained using a Bader charge analysis, which suggests that the yttrium doping changes average oxide basicity and influences hydration enthalpy in BCY. We then introduce a statistical thermodynamic model that predicts the hydration entropy of BCY at multiple dopant levels. Finally, the in silico enthalpy data and a priori derived entropy model is used to develop a relationship between the extent of material hydration and dopant concentration, temperature and pressure, which compares well to experimental hydration data. This work contributes toward a more fundamental understanding of perovskite hydration, aiding the rational design of proton conducting materials.

4.2 Methods

4.2.1 Computational Techniques

All DFT calculations were performed using the plane-wave pseudopotential method as implemented in the Vienna Ab-Initio Simulation Package (VASP). Plane waves with an energy cutoff of 400 eV were constructed using projector augmented wave (PAW) potentials. The generalized gradient approximation (GGA) was implemented using the PW91 exchange-correlation function.¹⁹ A 5 x 5 x 5 Monkhorst-Pack k-point mesh was used to sample the Brillouin zone.²⁰
A Bader charge analysis was used to determine oxide ion charge at each dopant level. This approach towards charge analysis is advantageous because it relies on the property of electron density alone and is not dependent on the basis sets or integration grids dictated for the simulations. In these calculations, the atoms are divided into subsystems at zero-flux surfaces, which enclose the Bader volume. The zero-flux surface is defined at the charge density minimum perpendicular to the surface of the atom. The charge of the atom is then approximated as the charge enclosed within the Bader volume.\textsuperscript{21}

### 4.2.2 Structural Considerations

All simulations maintained the conventional oxygen site restriction for high dopant concentrations, such that the number of oxygen sites per formula unit was restricted to three, thus following the relationship:\textsuperscript{4}

\[
[O^+_o] + [V^{3+}_o] + [OH^-_o] = 3
\] (4.2)

Furthermore, the unit cells for all yttrium dopant concentrations consisted of the minimum number of atoms to maintain electroneutrality. The chemical formula for yttrium-doped barium cerate is $\text{BaCe}_{1-x}Y_x\text{O}_{3-x/2}$, where $x$ is the mole fraction of the yttrium dopant. In order to obtain whole integer values, the number of atoms in a single unit cell of unhydrated yttrium-doped barium cerate was calculated as $\frac{2}{x}[\text{BaCe}_{1-x}Y_x\text{O}_{3-x/2}]$. The hydrated BCY material incorporated one water molecule into each unit cell resulting in cells composed of $\frac{2}{x}[\text{BaCe}_{1-x}Y_x\text{O}_{3-x/2}]\text{H}_2$. As an example, the unhydrated 50\% -doped BCY unit cell consisted of 4 $\text{Ba}^{2+}$ ions, 2 $\text{Ce}^{4+}$ ions, 2 $Y^{3+}$ ions, and 11 $\text{O}^{2-}$ for overall charge neutrality. For the hydrated case, the addition of one $\text{H}^{+}$ ion and one $\text{OH}^{-}$ ion maintained charge neutrality within the material, such that one unit cell was composed of $\text{Ba}_4\text{Ce}_2Y_2\text{O}_{12}\text{H}_2$. 
All dopant substitutions were assumed to occur on the cerium lattice sites, which is consistent with experimental data for low doping levels, though partial barium site substitution becomes more likely at high dopant concentrations. This study assumed 100% hydration of the barium cerate material. Although typical hydration of BCY ranges from 80-95% at temperatures of 500°C and below, this assumption allowed us to introduce one water molecule into each unit cell, which decreases the number of potential proton configurations and minimizes computational time.

The hydration properties of barium cerate at x = 0.5, 0.25, and 0.125 yttrium doping levels were evaluated in this study. Although experimental doping levels typically range from x = 0.01 - 0.2, our hydration studies were conducted with computationally tractable structures containing larger doping levels in order to provide smaller minimum supercell sizes. Barium cerate doped at 50%, 25%, and 12.5% yttrium concentrations provides a basis to study hydration trends within this material in a composition space that overlaps the experimentally-studied space, while minimizing computational time.

The lattice vectors for the unit cells were optimized for each dopant concentration in both the unhydrated and hydrated states by linearly expanding and compressing the lattice vector until the most favorable cell size was obtained. All vector changes were performed isotropically to minimize computational time. All atoms were allowed to relax during the simulations, which often caused the structure to become distorted due to octahedral tilting. This is a common phenomenon within perovskites, occurring when a protonic defect prompts slight material reorientation to garner a more favorable arrangement. The starting point for all optimizations was the experimentally determined ground state structure for undoped barium cerate. The experimentally and computationally calculated lattice parameters are displayed in Table 4.1 for
50%, 25%, and 12.5% yttrium doping in unhydrated BCY, using four $\text{BaCe}_{1-x} \text{Y}_x \text{O}_{3-\frac{x}{2}}$ formula units per unit cell. The resultant lattice constants deviated less than 1% from experimental values.

<table>
<thead>
<tr>
<th>Dopant Level</th>
<th>Lattice Parameter</th>
<th>Experimental (Å)</th>
<th>DFT (Å)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%</td>
<td>$a$</td>
<td>8.780</td>
<td>8.837</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>6.237</td>
<td>6.278</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>$c$</td>
<td>6.218</td>
<td>6.259</td>
<td>0.65</td>
</tr>
<tr>
<td>25%</td>
<td>$a$</td>
<td>8.780</td>
<td>8.855</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>6.237</td>
<td>6.291</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>$c$</td>
<td>6.218</td>
<td>6.272</td>
<td>0.86</td>
</tr>
<tr>
<td>12.5%</td>
<td>$a$</td>
<td>8.780</td>
<td>8.862</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>6.237</td>
<td>6.296</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>$c$</td>
<td>6.218</td>
<td>6.277</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 4.1 New lattice parameters calculated using DFT from the experimentally determined ground state structure for undoped barium cerate.\(^{23}\)

The hydration expansion was taken to be the difference between the lattice vectors of the hydrated and unhydrated states for each dopant concentration. An optimization curve was developed for both hydration states to depict how unit cell size influences relative material energy (Figure 4.1). Each polynomial curve fit was developed in Igor, a graphing and data analysis software tool, using the Levenberg-Marquardt algorithm to minimize the chi-square value. For both the unhydrated and hydrated states, three different configurational trials were averaged and the standard deviation was incorporated into the plot via error bars.
Figure 4.1 Geometric optimization of 50%-doped BCY unit cell. Relative energy as a function of unit cell size for unhydrated (solid curve) and hydrated (dashed curve) BCY. Points indicate the results of DFT calculations averaged over three configuration trials (standard deviations are depicted via error bars), and curves were obtained from quadratic least square fits.

4.2.3 Hydration Enthalpy Calculations

The hydration enthalpy of the material was calculated via:

$$\Delta H_{\text{hydration}} = 2\Delta E_{\text{OH}}^f - \Delta E_{\text{Vo}} - \Delta E_{\text{H}_2\text{O}}$$

consistent with previous literature.\(^{16}\) The energies of formation for two protonic defects ($\Delta E_{\text{OH}}^f$), an oxygen vacancy ($\Delta E_{\text{Vo}}^f$), and a water molecule ($\Delta E_{\text{H}_2\text{O}}^f$) are given as:

$$2\Delta E_{\text{OH}}^f = E_{\frac{1}{2}\{\text{BaCe}_{1-x}\text{Y}_{x}\text{O}_3\}\text{H}_2} - E_{\frac{1}{2}\{\text{BaCeO}_3\}} - \frac{1}{x}E_{\text{Y}} + \frac{1}{x}E_{\text{Ce}} - 2E_{\text{H}}$$

(4.4)

$$E_{\text{Vo}}^f = E_{\frac{1}{2}\{\text{BaCe}_{1-x}\text{Y}_{x}\text{O}_3\}_{\frac{1}{2}}} - E_{\frac{1}{2}\{\text{BaCeO}_3\}} - \frac{1}{x}E_{\text{Y}} + \frac{1}{x}E_{\text{Ce}} + E_{\text{O}}$$

(4.5)

$$\Delta E_{\text{H}_2\text{O}}^f = E_{\text{H}_2\text{O}} - 2E_{\text{H}} - E_{\text{O}}$$

(4.6)
where $x$ is the effective dopant concentration and $\mu$ is given as the chemical potential of the atom. Combining the above equations, the hydration enthalpy of the material at each dopant concentration was thus calculated by:

$$\Delta H_{\text{hydration}} = E_{\frac{1}{2}[\text{BaCe}_{1-x} \text{Y}_x \text{O}_3]H_2} - E_{\frac{1}{2}[\text{BaCe}_{1-x} \text{Y}_x \text{O}_{3-x/2}]} - E_{\text{H}_2\text{O}}$$ (4.7)

To carry out the enthalpy calculations, first the energies of unhydrated yttrium-doped barium cerate were determined for various arrangements of yttrium substitutions and oxygen vacancies. The most energetically stable configuration was then used towards the hydration enthalpy equation. A similar procedure was carried out for the hydrated material such that two hydrogen atoms were randomly placed throughout the unit cell to give a sampling of hydrated state energies. Unfortunately, due to computational limitations, every configurational microstate could not be sampled. Initially, a weighted average was calculated using the Boltzmann distribution. However, while the spread of energies for a specific macrostate was significant, about 60 kJ/mol (0.6 eV), the Boltzman weighted average fell within 0.001% of the most favorable energy value. Thus, the most energetically stable configuration for each state was deemed acceptable for use towards the hydration enthalpy calculation.

Since only the most stable configurations for the unhydrated and hydrated states are used towards the hydration enthalpy calculations, the prevalence of defect association within the material should not influence the accuracy of this model. At lower, more realistic dopant concentrations dopant association becomes more influential, such that it is more energetically favorable for protons to be located near the dopant atoms in the material.\textsuperscript{24,25} Although this proton configuration becomes more common at lower doping levels, the enthalpy model should still maintain accuracy because only the energies of the most favorable configurations are used.
All *ab initio* data was adjusted to compensate for temperature corrections by integrating the heat capacity curve of undoped barium cerate over temperature.\(^{26}\) The primary interest of this work lies in the development of perovskite materials for high temperature proton conductors, so all data analysis was done at a temperature of 800 K. The barium cerate heat capacity curve was thus integrated from 0 K, where the simulations took place, to 800 K leading to an increase in enthalpy of 83 kJ/mol (0.86 eV) in all simulations to account for thermal energy changes. The energy of water was also adjusted to account for temperature corrections by integrating the heat capacity of water over this temperature range. The enthalpy of water was calculated as -1390 kJ/mol (-14.4 eV) at 0 K and corrected as 1310 kJ/mol (-13.6 eV) at 800 K.

### 4.2.4 Hydration Entropy Model

A statistical thermodynamic model was developed to predict the hydration entropy of BCY at various dopant concentrations. The model was derived by considering the change of entropy due to the incorporation of one water molecule into a single unit cell of the material. While the vapor phase water molecule retained all translational, vibrational, and rotational degrees of freedom, the dissociated water molecule incorporated in the BCY lattice was assumed to have lost all of these degrees of freedom. Although there is likely a small vibrational contribution towards the entropy of BCY, as a first approximation, the entropy term from the vibrational degrees of freedom was neglected. Therefore, the only entropic contribution considered was the configurational entropy of the BCY material.

The most generalized equation for configurational entropy is given as:

\[
S = -R \sum (p_i \log p_i)
\]  

(4.8)
where $R$ is the gas constant and $p_i$ is the probability that the given microstate, $i$, exists. This probability can be determined via the Boltzmann distribution using the energy of the given state, such that

$$p_i = e^{-E/kT} / \sum e^{-E/kT}$$  \hspace{1cm} (4.9)

where the denominator, called the partition function $q$, requires the sampling of all potential configurational microstates.\footnote{27} For our most simple case, the 50\% Y-doped BCY material, this would require the calculation of 72 configurational arrangements of the unhydrated state and 288 combinations of the hydrated state. Unfortunately, this was too computationally expensive to achieve for this study, so we took a random sampling of the unhydrated and hydrated states for each dopant concentration. Since not every microstate could be studied, Equation 4.7 would not have given an accurate hydration entropy value for the fraction of the states that were sampled. Therefore, we had to use a more simplified version of Equation 4.7. If one assumes that every microstate is equally probable, Equation 4.7 collapses into the Boltzman entropy formula:\footnote{27}

$$S = R \log W$$  \hspace{1cm} (4.10)

where the multiplicity, $W$, is given as the number of possible configurational arrangements for one unit cell in either the unhydrated or hydrated state. Although this entropy model assumes equi-energetic microstates for all configurational arrangements, as a first pass approximation the model is still able to capture an important entropy trend within these doped perovskites. Errors induced by this model are discussed in detail below.

In order to derive a generalized equation for hydration entropy using Equation 4.9, the number of configurational arrangements had to be determined in terms of dopant concentration for both the unhydrated and hydrated states. First, in the unhydrated state, two yttrium atoms are
substituted for two cerium atoms in each unit cell. The number of possible combinations that two indistinguishable yttrium atoms can be incorporated into the unit cell is:

\[ W_Y = \frac{\left( \frac{x}{2} \right)!}{\left( \frac{x}{2} - 2 \right)!2!} \]  

(4.11)

where \( x \) is the dopant mole fraction. For every two yttrium atom substitutions, one oxygen vacancy forms. The number of potential configurations for an oxygen vacancy formation in a single unit cell is:

\[ W_{Vo} = \frac{6}{x} \]  

(4.12)

By considering these configurational combinations, the entropy of the unhydrated BCY system was derived as:

\[ S_{\text{unhydrated}} = R \log \left[ \frac{\left( \frac{x}{2} \right)!}{\left( \frac{x}{2} - 2 \right)!2!} \times \frac{6}{x} \right] \]  

(4.13)

For the hydrated state, one water molecule dissociates and is incorporated into each unit cell. The oxygen vacancy is filled by the hydroxyl ion of the dissociated water molecule, while the resulting proton initially bonds to an available oxygen ion. However, the protons are mobile and can take on a number of arrangements within a unit cell, where:

\[ W_H = \frac{\left( \frac{\alpha}{2} \right)!}{\left( \frac{\alpha}{2} - 2 \right)!2!} \]  

(4.14)

The number of potential yttrium permutations remains the same as in the unhydrated state, so the entropy of the hydrated material was calculated as:

\[ S_{\text{hydrated}} = R \log \left[ \frac{\left( \frac{\alpha}{2} \right)!}{\left( \frac{\alpha}{2} - 2 \right)!2!} \times \frac{\left( \frac{x}{2} \right)!}{\left( \frac{x}{2} - 2 \right)!2!} \right] \]  

(4.15)
Given the equation for change in entropy due to hydration:

\[ \Delta S_{\text{hydration}} = S_{\text{hydrated}} - S_{\text{unhydrated}} - S_{\text{H}_2\text{O}} \]  

(4.16)

the final expression to relate dopant concentration to hydration entropy is given as:

\[ \Delta S_{\text{hydration}} = R \log \left[ \frac{\left( \frac{x}{x-2} \right)!}{2!} \times \frac{x}{6} \right] - S_{\text{H}_2\text{O}} \]  

(4.17)

In this study, \( S_{\text{H}_2\text{O}} \) was taken to be the standard molar entropy of water vapor at 775 K, -188.84 J mol\(^{-1}\)K\(^{-1}\).\textsuperscript{28}

### 4.2.5 Degree of Hydration

The Gibbs free energy change due to hydration was calculated using the hydration enthalpy and entropy, such that

\[ \Delta G_{\text{hydration}} = \Delta H_{\text{hydration}} - T\Delta S_{\text{hydration}} \]  

(4.18)

Since the hydration enthalpy results are given in discrete values from the DFT simulations, the data was parameterized and a relationship between dopant concentration and hydration enthalpy was created in Igor using an exponential function to minimize the value of chi-square. The equilibrium constant for material hydration, \( K \), was then calculated using

\[ \Delta G_{\text{hydration}} = RT \ln K \]  

(4.19)

Finally, the degree of material hydration, \( X \), could be determined from the equilibrium constant via:

\[ X = \frac{K P}{1 + K P} \]  

(4.20)
where P is given as the partial pressure of water. This equation represents an a priori approach towards developing a relationship between the degree of BCY hydration and dopant concentration, temperature, and pressure.

4.3 Results and Discussion

4.3.1 Configurational Considerations

The most favorable configurations of the protons within the hydrated BCY material were determined for use in subsequent computational calculations. Previous experimental and computational studies reported that, within a perovskite material, protons bond approximately 1Å from an oxygen atom and, in their most favorable position, orient along the bisecting line between two oxide ions.\textsuperscript{6,7,9,11} Several alternative configurations were explored to determine the ideal proton position, including orienting the protons towards oxide ions in the BO\textsubscript{6} octahedron. However, the most favorable proton configurations occurred when the proton was oriented towards a neighboring oxide in one of the adjacent BO\textsubscript{6} octahedrons, forming a stabilizing hydrogen bond with the ion, in agreement with previous studies. A schematic representation of the potential proton positions is visualized in Figure 2a, first proposed by Hempelmann et al.\textsuperscript{29}
Figure 4.2 Proton orientations within BCY unit cell. a) Schematic illustration of the four potential proton positions around an oxide ion in a BCY perovskite material. The protonic defects (black) are bound approximately 1 Å from the oxide ion (white) and oriented along the bisecting line between two oxide ions. b) Schematic of two potential proton positions in a slightly distorted perovskite material. Of the two possible configuration illustrated, the proton would be oriented upwards to minimize the OH-O bond distance, 2.91 Å.

Since two protonic defects existed within each unit cell, a variety of factors were investigated to determine the most favorable positions of the two protons within a defined space. These factors included the distance between the two protons and the distance between the two oxide ions bonded to the protons, but no correlation between these two factors and the material’s energy was discovered. However, we did observe more favorable energies when the protonic defects were oriented towards the neighboring oxide ion that minimized the OH-O bond distance, illustrated in Figure 4.2b. As a result, each study was conducted by positioning the two protons around 20 different random combinations of oxygen ions within the unit cell, while always orienting the protons towards the nearest neighbor oxide ion. The only exception
occurred when 2 protons were to be directed towards the same oxygen atom, in which case the proton with the larger OH-O bond length was positioned towards its next nearest oxide ion. The calculated energies for each dopant concentration resulted in a spread of less than 60 kJ/mol (0.6 eV), where 50% of the data fell less than 20 kJ/mol (0.2 eV) above the most favorable energy values.

4.3.2 Hydration Expansion

The linear hydration expansions for 50%, 25%, and 12.5% yttrium-doped barium cerate were calculated as 0.8%, 0.4%, and 0.2%, respectively, which suggests a linear correlation between these two properties. This expansion of the unit cell is a result of the filling of oxygen vacancies (\(V'_O\)) by hydroxyl groups (OH\(^+_O\)) according to Equation 4.1, a phenomenon that is observed experimentally when the perovskite is exposed to a humid atmosphere.\(^{30}\) Since doping is responsible for the generation of oxygen vacancies and thus the incorporation of protonic defects, it was reasonable that the extent of material hydration correlates directly with dopant concentration in model systems. However, in real systems it is likely that this linear relationship tails off at high dopant concentrations due to defect association and an increase in A-site dopant substitution and lattice strain energy.

Understanding hydration expansion is critical to the development of ionic conducting membranes because brittle materials may crack or warp due to swelling during hydration, rendering them useless.\(^{31}\) While several sources attest to the importance of studying material expansion due to the incorporation of protonic defects, few studies explain how hydration expansion is influenced by dopant concentration.\(^{4,31,32}\) However, studies of common perovskite materials have reported similar hydration expansions to those above. Kreuer has measured a
0.4% hydration expansion in 15% yttrium-doped barium zirconate (BaZrO$_3$),$^4$ while Martorana published a hydration expansion of 0.4% for BCY with an unknown yttrium dopant concentration.$^{33}$ The lack of published data pertaining to this important design parameter highlights the necessity for further experimental and quantum mechanical studies of perovskite expansion due to material hydration.

4.3.3 Hydration Enthalpy

The hydration enthalpies of BaCe$_{1-x}$Y$_x$O$_{3-x/2}$ at $x = 0.5$, 0.25, and 0.125 were calculated as -211 kJ/mol (-2.19 eV), -205 kJ/mol (-2.12 eV), and -180 kJ/mol (-1.87 eV), respectively. These enthalpies were determined using the most favorable configurations of the unhydrated and hydrated state for each dopant concentration. Figure 4.3 compares the BCY hydration enthalpies determined from this study to the results of several thermal gravimetric analysis (TGA) experiments completed by Kreuer and Coors.$^5,13,14$ The in silico data trends very well with the experimental studies. As predicted, the hydration enthalpy becomes more negative at higher dopant concentration, i.e. material hydration becomes more thermodynamically favorable with increased doping levels.
Figure 4.3 Hydration enthalpy vs. dopant concentration. Hydration enthalpy of BCY as a function of yttrium dopant concentration. Solid points represent data gathered from this computational study, while hollow markers signify data gained from previous TGA experiments: □-Kreuer, 4 △-Kreuer, 14 O-Coors. 13 The dotted line denotes an exponential curve fit in Igor to minimize the value of chi-square; this curve was used for subsequent equilibrium constant calculations.

This hydration trend has been attributed in literature to variations in the lattice energy and changes in oxide basicity at different dopant levels. 5,14,34 The latter phenomenon has been explored in this study by calculating the charges of the oxide ions throughout the lattice using Bader charge analysis. Since the electronegativity of Y³⁺ is less than that of Ce⁴⁺, it was predicted that the material with higher yttrium concentrations would yield a more negative average oxide charge. In the 50% doped material, every oxide ion is coordinated to one yttrium and one cerium ion, while in 25% and 12.5% yttrium-doped BCY only one-half and one-quarter of the oxide ions are bonded to a yttrium ion, respectively. Therefore, it is expected that the
oxide ions in the 50% doped material would have a greater average negative charge because the oxygen ions retain more of their electrons when coordinated with the yttrium dopant.

The results of the Bader charge analysis reveals a linear correlation between dopant concentration and average oxygen charge, where the average oxide charge was found to be -1.31e, -1.28e, and -1.26e at 50%, 25%, and 12.5% doping levels, respectively. As predicted, the average oxide charge becomes more negative with increasing dopant concentration, thus yielding an increase in oxide basicity at higher doping levels. This data supports Kreuer’s postulate that more negatively charged oxide ions lead to increased $\text{OH}_o^-$ bond strengths, causing an energetic stabilization of protonic defects and a more favorable hydration enthalpy.\(^5\)

Further investigation into the oxide basicity revealed how oxide ion charge is dependent on the coordination to yttrium ions. Oxide ions coordinated to a single Y ion had a charge of -1.32e with a standard deviation of 0.03e, whereas those coordinated to no Y ions had a charge of -1.25e with a standard deviation of 0.03e. A one sided t-test concluded that the charge of oxide ions coordinated to a yttrium ion is significantly more negative than those coordinated to only cerium ions. The excess electronic charge of 0.07e due to Y coordination calculated in this study is less than Kreuer’s reported value of 0.13e. The disparity between these values is most likely due to the differences between the Bader charge analysis used in this study and Kreuer’s Mulliken population analysis, which is dependent on the basis sets of the simulation.\(^{21}\)

### 4.3.4 Hydration Entropy

A statistical thermodynamic model was developed based solely on the configurational entropy of BCY and the standard molar entropy of water (for details pertaining to the development of this model refer to Section 2.4). Figure 4.4 depicts a plot of Equation 4.17,
which describes the relationship between dopant concentration and hydration entropy, and includes BCY hydration entropy data obtained from a TGA experiment. The entropy model demonstrates that hydration entropy decreases with increasing dopant concentration. This suggests that higher levels of doping lead to a decrease in configurational entropy, and a corresponding decrease in the entropic favorability of material hydration.

![Graph showing hydration entropy vs dopant concentration](image)

**Figure 4.4 Hydration entropy vs. dopant concentration.** The statistical thermodynamic model (solid line) plotted against experimental measurements (●)\(^5\) of the hydration entropy.

While this simplified model captures the same entropy trend seen experimentally,\(^5\) it fails to capture quantitatively the entropy loss that occurs upon material hydration. There are several likely sources of error in this model. First, as stated previously, this model only considers the configurational contribution toward hydration entropy. One likely source of error is the exclusion of vibrational entropy from this simplified model\(^22\). The oxygen vacancies within the unhydrated
material enable increased lattice vibrational modes to be expressed, which are then suppressed upon material hydration. Accounting for this vibrational entropy would increase entropy in the unhydrated materials, causing a decrease in the change in entropy upon hydration. Including the vibrational entropy contribution may lend towards better agreement between the model and experimental results.

Additionally, recent evidence of proton trapping around dopant ions indicates that the probability of every lattice site being occupied is not equal. Proton trapping implies that protons are more stable when bonded to dopant-coordinated oxygen ions and require an additional activation energy to escape the local dopant environment. In the model presented here, we make a significant assumption that proton bonding throughout the lattice is equally probably on every oxygen site. However, experimental\textsuperscript{15,35} and computational\textsuperscript{10,17,36,37} data demonstrating proton trapping within various perovskite materials suggests that this statistical thermodynamic model is not accurate. If the model were to account for the limited proton-accessible states in the hydrated perovskite, entropy of the hydrated material would decrease and the change in entropy due to hydration would also shift down, leading to a better agreement between the entropy model and experimental results. Unfortunately, no existing data outlines the extent of proton trapping within yttrium-doped barium cerate, so as of now this contribution cannot be updated within the given model.

Although refinements to the present theoretical model are needed to improve accuracy, the current statistical thermodynamic approach does capture an important general trend between the hydration entropy and dopant concentration. As the dopant level increases, the hydration entropy becomes more negative, leading to an entropic destabilization of the protonic defects.
This highlights a thermodynamic tradeoff between more favorable hydration enthalpies and less favorable hydration entropies as the dopant concentration increases.

4.3.5 Degree of Hydration

The results from the previous hydration enthalpy and entropy study suggest competing effects between hydration enthalpy and entropy in determining the overall thermodynamic favorability of perovskite hydration as a function of doping level. By combing the curve fit for the DFT enthalpy data with the statistical thermodynamics entropy model, the change in Gibbs free energy as a result of material hydration was determined as a function of dopant concentration and temperature. According to the results, plotted in Figure 4.5, hydration enthalpy dominates at low concentrations, where the change in Gibbs free energy continues to become more negative, or more favorable, with increasing dopant concentration. The unfavorable hydration entropy begins to dominate at about 29% doping, at which point an increase in dopant concentration leads to increasing, or less favorable, change in Gibbs free energy. Additionally, material hydration becomes less thermodynamically favorable with increasing temperature because the unfavorable entropy term dominates at higher temperature values.
Figure 4.5 Gibbs free energy vs. dopant concentration. Plot of the change in Gibbs free energy due to hydration as a function of dopant concentration at three different temperatures: 800 K (solid line), 1000 K (dashed line), 1200 K (dash-dot line).

Once an equation for $\Delta G$ was derived, a relationship between the degree of material hydration and dopant concentration, temperature, and pressure was developed using Equations 4.19 and 4.20. A plot of the resulting equation (Figure 4.6a) displays the competing thermodynamic effects between hydration enthalpy and entropy displayed in the above plot. Here, we see that material hydration increases with increasing dopant concentration until a doping level of about 25% is reached. At this point, material hydration begins to recede with increased doping. This finding suggests that there is an optimal dopant concentration that could maximum material hydration within BCY. However, there is no experimental data to validate this result because it is difficult to synthesize perovskites with dopant concentrations higher than 25% due to dopant substitution on the A-lattice site at high doping levels.\textsuperscript{4}
While the hydration model derived here from solely first principles techniques displays the same sigmoidal trend seen in experimentally, there is a large discrepancy between the temperatures at which we predict BCY will be hydrated and those seen in experimental studies. The dehydration temperature ($T_c$), defined as the temperature where dehydration and hydration occur at equal rates, can be used to compare our model to experimental data. At 15% yttrium doping, Kreuer\textsuperscript{5} and Coors\textsuperscript{13} reports a $T_c$ of 700°C and 800°C within BCY from TGA experiments, respectively. According to the model presented here, the $T_c$ for 15%-doped BCY is about 1200°C. The large quantitative discrepancy between the computational model presented here and the experimental data likely lies in the inaccuracy of the hydration entropy model. If the hydration entropy model were to shift more negative, toward the experimentally-derived data,
the unfavorable hydration entropy term would dominate at lower temperatures. This would cause the hydration model in Figure 4.6 to shift left toward experimental hydration curves.

Despite discrepancies between the theoretical and experimentally derived hydration curves, the development of this hydration model using purely *in silico* techniques and a priori principles can still be beneficial for the improvement of ionic conducting perovskite materials. Since hydration curves give important insight into the material’s ability to incorporate protonic defects, this approach may contribute towards the rational design of doped-perovskite oxides. For example, the methodology may be useful for screening for potentially favorable perovskite-dopant combinations or understanding how dopant concentration influences thermodynamic hydration properties.

### 4.4 Conclusion

Yttrium-doped BaCeO$_3$ serves as a model compound for perovskite oxide studies because of its rapid proton conduction capabilities and the vast breadth of data available pertaining to hydration and defect equilibrium within the oxide. Using Density Functional Theory, this work has expanded upon previous quantum mechanical hydration studies of perovskite materials by probing how dopant concentration influences hydration properties of BCY, while in the process verifying and gaining a deeper understanding of several experimental trends.

The hydration expansion of BCY correlated linearly with dopant concentration, suggesting that the extent of oxygen vacancies influences material swelling. In agreement with experimental results, the hydration enthalpy of BCY became more favorable with increasing dopant levels. A Bader charge analysis revealed that an increase in dopant concentration led to an overall increase in oxygen basicity, leading to a possible stabilization of protonic defects.
These results suggest that dopant concentration directly affects oxygen charge, which contributes to thermodynamic changes of the hydration enthalpy. Next, a statistical thermodynamic model was developed that depicts the trend between dopant concentration and hydration entropy. Also consistent with experiments, this model predicts that hydration entropy becomes more negative with increasing dopant levels, exposing a thermodynamic tradeoff between hydration enthalpy and entropy at varying dopant concentrations. Finally, by utilizing the developed hydration enthalpy and entropy models, a relationship between the degree of material hydration and dopant concentration, temperature, and pressure was developed. The resultant plots indicate an optimal dopant level for maximum material hydration within yttrium-doped barium cerate. In this study we have demonstrated, for the first time, an analysis that was conducted using solely a priori methods to predict hydration behavior in perovskite oxides, an approach that can be improved upon and utilized in the future for the rational design of ionic conducting perovskite materials.

4.6 References


CHAPTER V

FIRST PRINCIPLES STUDY OF THE STABILITY OF ORTHORHOMBIC BaCeO3 SURFACES

5.1 Introduction

Since Iwahara’s discovery of perovskite-type materials in 1983, these ceramic oxides have been explored as efficient high temperature proton conductors in numerous electrochemical devices, such as batteries, fuel cells, and sensors. Researchers have recently become interested in utilizing these materials in low (100-300°C) and intermediate temperature (300-600°C) applications, where the energy and cost for heating is reduced. Unfortunately, at these temperature ranges low grain boundary conductivity greatly limits the overall conductivity across these ceramic membranes. Researchers hypothesize the origin for slow proton conduction in this region arises from a positive grain boundary core charge that results from the segregation of positively charged defects, such as oxygen vacancies, to the grain boundary interface. While the development of a positive grain boundary core charge would repel protons away from the grain interface and decrease conduction across the region, little information is available detailing the evolution of this core charge. Thus, significant
experimental and theoretical work has shifted to determining the cause and mitigating the source of low grain boundary conductivity.

While new work has been published trying to model the grain-grain boundary of various perovskites, it is difficult to isolate specific causes for proton and defect segregation at these complex interfaces.\textsuperscript{12-14} One means of simplifying the study of this interface is to consider a perovskite-vacuum interface. While this model may not include important grain-grain interactions, it provides a system in which fundamental driving forces for defect segregation can be explored. In order to carry out these foundational studies, the stability of various perovskite-vacuum surfaces must first be established to identify reasonable surfaces on which to carry out these interfacial studies.

In addition to providing a stable model in which to probe defect segregation, a surface stability study of perovskite-vacuum interfaces may also yield important structural and electronic information for new, alternative perovskite applications. For example, studies have demonstrated that perovskite surfaces exhibit high catalytic activity for a variety of chemical reactions, including oxygen reduction,\textsuperscript{15,16} hydrocarbon activation,\textsuperscript{17} and hydrogen evolution.\textsuperscript{18} The performance of perovskite-type oxide catalysts is related directly to the configurational and electronic structure of the perovskite surface, further motivating recent experimental and theoretical studies that probe the stability and structure of perovskite surfaces.

Within the broad class of ABO\textsubscript{3} perovskite-oxides, barium cerate (BaCeO\textsubscript{3}) has exhibited amongst the highest proton conductivities and has shown promise as a catalyst or catalyst support for numerous chemical reactions.\textsuperscript{4,19} It is therefore important to establish stable surfaces of BaCeO\textsubscript{3} on which subsequent theoretical studies can take place. The II-IV perovskites, such as BaCeO\textsubscript{3}, can be cleaved along numerous surface facets. The (001), (110), and (111) surface...
facets represent the most densely packed of these potential surfaces. Within each of these facets the perovskite may be cleaved to reveal two complementary surfaces, as there are two repeating layers perpendicular to the material interface. The (001) facet is categorized as a non-polar surface because the replicating layers, BaO and CeO₂ in the case of BaCeO₃, retain a net-neutral charge. On the other hand, cleavage along the (110) and (111) facets result in polar surfaces as the repeating layers take on a non-zero charge, resulting in the formation of a dipole moment perpendicular to the surface.²⁰,²¹

A multitude of theoretical studies completed on various perovskite oxides reveal that the non-polar (001) surface facet most often exhibits a lower surface energy than the polar (110) and (111) facets.²²-²⁴ Since a reduction in surface energy indicates enhanced stability, these findings suggest that the (001) facet is the most stable surface of those probed. The results of a recent study completed by Shishkin and Ziegler found that this trend holds true for rhombohedral BaCeO₃.²⁵

While the (001) surface has garnered much attention for its low energy surface, much interest has focused on the unique properties of the polar surfaces. There are several techniques in which surfaces can cancel out polarization to reduce the destabilizing effects of the macroscopic dipole moment perpendicular to the material surface. First, the surface may be stabilized through charge compensation, such that the surface layer takes on a charge density:

$$\sigma' = \sigma R_2/(R_1+R_2)$$  (5.1)

where \(\sigma\) represents the charge density of a layer of bulk material and \(R_1\) and \(R_2\) signify the interlayer spacing. This compensation can be attained through the deletion of surface atoms or the introduction of foreign atoms or ions into the surface layer. Since the surface structure differs from the layers found in the perovskite bulk, these surfaces are defined as non-stoichiometric.
surfaces. Alternatively, charge compensation may be accomplished through the redistribution of electrons in response to the polar electrostatic field. In this manner, a stoichiometric polar surface may be maintained by repositioning electrons within the atoms at the material surface. For example, Noguera observed a shift in the density of states of electrons in the bulk SrTiO$_3$ compared to the Ti-terminated SrTiO$_3$, providing evidence for favorable electron redistribution at the perovskite surface to mitigate surface instabilities.$^{20}$

The method each material uses to stabilize polar surfaces is dictated primarily by energetic considerations. For perovskite oxides, many researchers have found that non-stoichiometric terminations of the (110) and (111) surfaces have resulted in surface energies approaching that of the (001) surface, suggesting that surface reconfiguration is the energetically favorable method of polarization compensation in perovskite oxides.$^{24,26,27}$ These findings motivate the continued study of both non-polar and polar surface terminations of perovskite oxides.

In this work, the cleavage energies of the (001), (110), and (111) surface facets of orthorhombic BaCeO$_3$ are probed to identify the most stable surface structure. Additionally, the stabilities of stoichiometric surfaces are compared to the non-stoichiometric polar surfaces to identify how orthorhombic BaCeO$_3$ compensates for polarity effects. Finally, two different computational techniques are performed and compared to identify how method influences surface stability results. The results of this study were used to identify the surfaces and parameters used in subsequent BaCeO$_3$-vacuum studies completed in Chapter 6 of this thesis.
5.2 Methods

5.2.1 Computational Techniques

All DFT calculations were carried out using the plane-wave pseudopotential method as implemented by the Vienna Ab-Initio Simulation Package (VASP). For this study plane waves with an energy cutoff of 520 eV were constructed using projector augmented wave (PAW) potentials. The generalized gradient approximation (GGA) was applied using the PW91 exchange correlation functional. A 6 x 6 x 1 Monkhorst-Pack sampling of the Brillouin zone was utilized for all surface calculations, while a 6 x 6 x 6 k-point mesh was employed for bulk calculations.

It is well understood that for many transition metals, such as cerium, the GGA functional within the DFT framework fails to cancel the Coulomb interactions between localized d- and f-electrons. This leads to erroneous estimations of material properties, such as band gap, due to inaccurate predictions of the electronic band structure and charge distribution. One method to overcome this limitation is to employ a Hubbard correction term, U, which acts to improve the Coulomb self-interaction potential. While several studies have shown improvement in predicting electronic properties of BaCeO₃, CeO₂, and CeO₃ by including a Hubbard correction term to Ce to properly localize the 4f electrons, the most appropriate value of U is still widely debated. Since the value cannot be calculated directly, it must be fit to experimentally measured material properties, such as band gap or defect formation energy, leading to a wide range of useable U values.

For perovskite oxide surface energy calculations, many DFT studies omit the Hubbard correction term, while others choose to apply the DFT+U approach. In this study, we compare the surface energy values of each BaCeO₃ termination using both the DFT and the
DFT+U methodologies. We use a value of $U = 11 \text{ eV}$ to reproduce the experimental band gap of BaCeO$_3$, consistent with previous barium cerate DFT+U studies.$^{34}$ The DFT+U method results in a calculated band gap of 352 kJ/mol (3.65 eV), within the range of experimental values, while DFT underpredicts the BaCeO$_3$ band gap at 216 kJ/mol (2.24 eV).

### 5.2.2 Surface Calculations

We calculated the geometrically optimized ideal bulk structure of orthorhombic BaCeO$_3$ using a supercell consisting of 4 chemical formula units. The lattice constants obtained computationally were $a = 8.942 \text{ Å}$, $b = 6.356 \text{ Å}$, and $c = 6.336 \text{ Å}$, compared to the experimental values of $a = 8.780 \text{ Å}$, $b = 6.237 \text{ Å}$, and $c = 6.218 \text{ Å}$.

The surfaces were constructed from the optimized bulk geometries using a slab model, whereby a vacuum gap was introduced into the unit cell to artificially form a material surface upon unit cell replication. In the slab model, the surfaces may be structured in both a symmetric and an asymmetric arrangement. In the symmetric system, an odd number of layers are configured such that the terminated surfaces are identical on opposite sides of the slab in the $z$-direction. Symmetrical slabs are often utilized in surface stability studies to cancel out any dipole moments that develop in the polar surfaces. On the other hand, an asymmetric slab consists of an even number of layers where the opposite surfaces are constructed of the two different complementary surfaces. For this study we created both an 11-layer symmetric slab and a 12-layer asymmetric slab of the stoichiometric surfaces of the (001), (110), and (111) facets to compare how slab construction influences stability outcomes. Furthermore, we formed 11-layer symmetric slabs of the non-stoichiometric surfaces that fulfill the charge compensating criteria detailed in Equation 5.1 for the polar (110) and (111) facets. To mitigate any spurious
interactions between cells, a vacuum gap of 10 Å was introduced between each slab. All surface slabs are depicted in Figure 1.

Surface stability was measured by calculating cleavage energy, which corresponds to the energy required to split a crystal into two complementary surfaces, and surface relaxation energy, which is the favorable energy reduction that takes place once the cleaved surface is allowed to relax. Since the symmetric slabs do not retain an overall stoichiometric composition, the cleavage energy must be calculated by averaging the energies of the two complementary slabs, given as:

$$E_{cl}(\alpha + \beta) = \frac{1}{2S}[E_{slab}^{fixed}(\alpha) + E_{slab}^{fixed}(\beta) - \frac{n}{m}E_{bulk}]$$

(5.2)

where $E_{slab}^{fixed}$ is the total energy of the unrelaxed termination, $E_{bulk}$ is the energy of the bulk BaCeO$_3$, $n$ is the total number of chemical formula units in the $\alpha$- and $\beta$-terminated slabs combined, and $m$ is the number of chemical formula units in the bulk supercell. The variables $\alpha$ and $\beta$ denote complementary terminations, $S$ is the surface area, and $1/4$ represents the four surfaces created upon cleavage of the crystal. To calculate the cleavage energy for the symmetric, non-stoichiometric surfaces that are self-complementary, the following equation was used:

$$E_{cl}(\alpha) = \frac{1}{2S}[E_{slab}^{fixed}(\alpha) - \frac{n}{m}E_{bulk}]$$

(5.3)

where $n$ now represents the number of chemical formula units in the single slab.

Since the asymmetric slabs retain an overall stoichiometric chemical composition, the cleavage energy could be calculated more simply, as:

$$E_{cl}(\alpha + \beta) = \frac{1}{2S}[E_{slab}^{fixed}(\alpha/\beta) - \frac{n}{m}E_{bulk}]$$

(5.4)
where $\alpha/\beta$ represents the asymmetric slab. $n$ now equals the total number of chemical formula units in the single asymmetric slab and the equation only needs to be divided by 2 to calculate the average cleavage energy.

While $E_{cl}$ represents the average energy per surface to cleave a BaCeO$_3$ crystal into two surfaces, allowing the surfaces to relax enabled us to differentiate between the stability of the two complementary surfaces. Within the 11-layered slab, the middle three layers were kept frozen to reproduce the bulk material while the outer four layers were allowed to relax. The relaxation energies for each surface were calculated by:

$$E_{relax}(\alpha) = \frac{1}{25}[E_{slab}^{relax}(\alpha) - E_{slab}^{fixed}(\alpha)]$$

where $E_{slab}^{relax}(\alpha)$ represents the energy of the given slab after relaxation.

Finally, the surface energy of each termination was calculated as the sum of the cleavage and relaxation energies:

$$E_{surface}(\alpha) = E_{cleavage}(\alpha + \beta) + E_{relaxation}(\alpha)$$

$$E_{surface}(\beta) = E_{cleavage}(\alpha + \beta) + E_{relaxation}(\beta)$$

**5.3 Results and Discussion**

**5.3.1 Symmetric vs. Asymmetric Slab Results**

Table 5.1 displays the average cleavage energies, J/m$^2$, for the stoichiometric (001), (110), and (111) surface facets arranged in both the symmetric and asymmetric slab configurations. The average energies (reported per surface) required to cleave the BaCeO$_3$ crystal along its (001) facet are calculated as 0.89 J/m$^2$ and 0.88 J/m$^2$ for the symmetric and asymmetric slabs, respectively. The difference between these values, approximately 1%, is insignificant, indicating that either the asymmetric or symmetric system is satisfactory for
exploring this non-polar surface. On the other hand, the average cleavage energies for the two polar surfaces depend more heavily on the slab configuration. The (111) results reveal that the asymmetric slab produces a cleavage energy 0.08 J/m² lower than the symmetric system. For the (110) surface facet, the asymmetric slab yields a 0.24 J/m² greater cleavage energy than its symmetric counter part. As a means of comparison, surface energies for metals typically range between 0.1 and 3 J/m². Thus, differences in cleavage energies of 0.1-0.24 J/m² are significant contributions toward the energy required to reveal these two surfaces.

For both the symmetric and asymmetric slab systems, the same stability trend is obtained. The non-polar (001) facet requires the least amount of energy to reveal the complementary (001) surfaces, followed by the (111) and (110) facets. However, the quantitative values for the polar surfaces vary depending on the slab system. This is likely due to the dipole moments that are generated normal to the perovskite surface. To avoid any dipole moment that may arise across the slab, a symmetric configuration was used for all subsequent surface studies.

<table>
<thead>
<tr>
<th></th>
<th>Symmetric</th>
<th>Asymmetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>0.89</td>
<td>0.88</td>
</tr>
<tr>
<td>(110)</td>
<td>2.64</td>
<td>2.88</td>
</tr>
<tr>
<td>(111)</td>
<td>2.46</td>
<td>2.38</td>
</tr>
</tbody>
</table>

**Table 5.1 Average cleavage energies of BaCeO₃ surfaces.** The average cleavage energies (J/m²) of the stoichiometric (001), (110), and (111) surface facets arranged in symmetric and asymmetric slabs

**5.3.2 DFT vs. DFT+U results**

The cleavage energies for both the stoichiometric and non-stoichiometric surface facets calculated using the DFT and DFT+U methodologies are presented in Table 5.2. The results between the two computational techniques vary significantly for all of the tested surfaces except
for the non-stoichiometric Ba+ CeO (110) surface. While most of the surfaces reveal higher calculated cleavage energies using the DFT method compared to the DFT+U technique, the BaO₂ + O (111) surface exhibits a higher cleavage energy with the DFT+U methodology. Thus, the addition of the Hubbard constant does not yield a consistent change in the cleavage energies across different surfaces. Despite this inconsistency, the stability trends of the surfaces tested here do not vary with the chosen technique. Using both traditional DFT and DFT+U, the surface stability decreases as: (001) BaO + CeO₂, (110) O + O, (110) Ba + CeO, (111) BaO₂ + O, (111) Ce + Ce, (111) BaO₃ + Ce₂, (110) BaCeO + O₂.

Table 5.2 Average cleavage energies of BaCeO₃ surfaces using different computation methodologies. Average cleavage energies (J/m²) of the stoichiometric and non-stoichiometric (001), (110), and (111) surface facets using the DFT and DFT+U methodologies

<table>
<thead>
<tr>
<th>Surface</th>
<th>DFT</th>
<th>DFT + U</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) BaO + CeO₂</td>
<td>0.89</td>
<td>0.85</td>
</tr>
<tr>
<td>(110) BaCeO + O₂</td>
<td>2.64</td>
<td>2.44</td>
</tr>
<tr>
<td>(110) Ba + CeO</td>
<td>1.66</td>
<td>1.66</td>
</tr>
<tr>
<td>(110) O + O</td>
<td>1.64</td>
<td>1.38</td>
</tr>
<tr>
<td>(111) BaO₃ + Ce₂</td>
<td>2.46</td>
<td>2.05</td>
</tr>
<tr>
<td>(111) BaO₂ + O</td>
<td>1.66</td>
<td>1.70</td>
</tr>
<tr>
<td>(111) Ce + Ce</td>
<td>2.13</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Since no experimental data exists with which to compare these computational results, it is difficult to say which of these two techniques offers the most accurate quantitative prediction of surface stability. Furthermore, these results reveal that the value of the Hubbard constant, U, also influences that the cleavage energy values. For example, Shishkin and Ziegler chose a much smaller Hubbard constant of U=5 to complete their surface stability studies. They chose this value because instead of aiming to adequately predict material band gap they chose to accurately
describe the formation of defect states within BCY. Comparing the quantitative values found here, using \( U = 11 \), with those reported by Shishkin and Ziegler, who used \( U = 5 \), it is clear that the value of \( U \) chosen alters the quantitative value of the calculated cleavage energeries (Table 5.3).

If experimental values of cleavage energy existed with which to fit the \( U \) parameter to, this methodology may prove to be more accurate than the traditional DFT method. However, as no experimental data currently exists regarding the cleavage energies of these perovskite surface facets, it is no more accurate and more computationally expensive to use the DFT+U technique. Thus, for the remainder of these surface studies, the traditional DFT methodology will be employed.

<table>
<thead>
<tr>
<th></th>
<th>( U = 11 )</th>
<th>( U = 5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) ( \text{BaO} + \text{CeO}_2 )</td>
<td>4.26</td>
<td>6.96</td>
</tr>
<tr>
<td>(101) ( \text{BaCeO} + \text{O}_2 )</td>
<td>12.26</td>
<td>19.52</td>
</tr>
<tr>
<td>(111) ( \text{BaO}_3 + \text{Ce}_2 )</td>
<td>10.29</td>
<td>18.31</td>
</tr>
</tbody>
</table>

**Table 5.3 Comparison of average cleavage energies using two disparate Hubbard correction terms.** Average cleavage energies (J/m\(^2\)) of the stoichiometric (001), (110), and (111) surface facets using \( U = 11 \) (as reported in this paper) and \( U = 5 \) (as reported by Shishkin et. al.)\(^{25} \).

### 5.3.3 Surface Stability Results

The calculated cleavage, relaxation, and surface energy results are shown in Table 5.4 for all surface terminations using a symmetric slab configuration and the traditional DFT methodology. The (001) surface facet yielded the lowest cleavage energy, indicating that it requires the least amount of energy to break the chemical bonds during crystal cleavage. These results support the findings of Shishkin and Ziegler, who observed the same trend for rhombohedral \( \text{BaCeO}_3 \) surfaces. To justify this result, the authors calculated the number of broken bonds associated with the formation of each of the three surface facets. They determined
that fewer bonds are cleaved to reveal the (001) surface than the (110) and (111) terminations, and thus concluded that the (001) facet should require less energy for its creation.\textsuperscript{25} Our study further builds upon Shishkin and Ziegler’s work by probing the stability of specific terminations and stoichiometries of BaCeO\textsubscript{3} surfaces by incorporating relaxation energy into the stability study.

<table>
<thead>
<tr>
<th>Termination</th>
<th>E\textsubscript{el}</th>
<th>E\textsubscript{relax}</th>
<th>E\textsubscript{surf}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaO</td>
<td>0.89</td>
<td>-0.20</td>
<td>0.69</td>
</tr>
<tr>
<td>CeO\textsubscript{2}</td>
<td>0.89</td>
<td>-0.18</td>
<td>0.72</td>
</tr>
<tr>
<td>(110)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaCeO\textsubscript{2}</td>
<td>2.64</td>
<td>-0.40</td>
<td>2.24</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>2.64</td>
<td>-0.96</td>
<td>1.68</td>
</tr>
<tr>
<td>CeO</td>
<td>1.66</td>
<td>-0.49</td>
<td>1.16</td>
</tr>
<tr>
<td>Ba</td>
<td>1.66</td>
<td>-0.81</td>
<td>0.85</td>
</tr>
<tr>
<td>O</td>
<td>1.64</td>
<td>-0.88</td>
<td>0.76</td>
</tr>
<tr>
<td>(111)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaO\textsubscript{3}</td>
<td>2.46</td>
<td>-0.65</td>
<td>1.81</td>
</tr>
<tr>
<td>Ce</td>
<td>2.46</td>
<td>-0.40</td>
<td>2.06</td>
</tr>
<tr>
<td>BaO\textsubscript{2}</td>
<td>1.66</td>
<td>-0.77</td>
<td>0.89</td>
</tr>
<tr>
<td>O</td>
<td>1.66</td>
<td>-0.72</td>
<td>0.94</td>
</tr>
<tr>
<td>Ce\textsubscript{0.5}</td>
<td>2.13</td>
<td>-1.22</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Table 5.4 Surface energies of various BaCeO\textsubscript{3} surface terminations. The cleavage, relaxation, and surface energies (J/m\textsuperscript{2}) of the stoichiometric and non-stoichiometric (001), (110), and (111) BaCeO\textsubscript{3} surface facets.

While both the (110) and (111) surface facets require a higher cleavage energy than the (001) facet, the non-stoichiometric terminations of these polar surfaces require less energy to cleave than the stoichiometric terminations. Furthermore, these surfaces demonstrate higher absolute relaxation energies compared to the (001) surfaces, indicating that there is more reconfiguration occurring at these surfaces upon crystal cleavage. This is evidenced in Table 5.5, which depicts the average atomic displacement that occurs perpendicular to the surface for each atom in the four relaxed layers of the slab. The relaxation results show greater displacement from
the ideal structure in the nonstoichiometric (110) and (111) surfaces compared to the (001) surface, supporting the relaxation energy results. Previous studies have also observed greater relaxation in the non-stoichiometric surfaces due to a reduction in the coordination number for atoms at the surface.\textsuperscript{23,26} Our observations support these results when comparing non-stoichiometric surfaces and the stoichiometric surfaces from which they are formed. For example, the BaO\textsubscript{2}- and O- terminated (110) surfaces are obtained by stripping away O or Ba & O atoms, respectively, from the stoichiometric BaO\textsubscript{3}- terminated surface. Comparing the atomic relaxation for these three surfaces, there is a greater deviation from the ideal lattice positions for the non-stoichiometric BaO\textsubscript{2}- and O- surfaces, although the degree of divergence is larger at the surface and tapers quickly moving into the bulk material.

<table>
<thead>
<tr>
<th>Layer</th>
<th>BaO-terminated surface</th>
<th>CeO2-terminated surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaO</td>
<td>Ba(-0.18) O(0.09)</td>
<td>CeO2 Ce(0.06) O(-0.11)</td>
</tr>
<tr>
<td>CeO2</td>
<td>Ce(0.12) O(0.07)</td>
<td>BaO Ba(0.24) O(0.14)</td>
</tr>
<tr>
<td>BaO</td>
<td>Ba(0.01) O(0.05)</td>
<td>CeO2 Ce(0.07) O(0.04)</td>
</tr>
<tr>
<td>CeO2</td>
<td>Ce(0.04) O(0.01)</td>
<td>BaO Ba(0.09) Ce(0.05)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Layer</th>
<th>BaCeO-terminated surface</th>
<th>O2-terminated surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCeO</td>
<td>Ba(0.07) Ce(0.06) O (-0.32)</td>
<td>O2 O(-0.43)</td>
</tr>
<tr>
<td>O2</td>
<td>O(0.25)</td>
<td>BaCeO Ba(-0.14) Ce(0.19) O(0.33)</td>
</tr>
<tr>
<td>BaCeO</td>
<td>Ba(-0.14) Ce(0.03) O (-0.10)</td>
<td>O2 O(-0.10)</td>
</tr>
<tr>
<td>O2</td>
<td>O(0.11)</td>
<td>BaCeO Ba(-0.02) Ce(0.06) O(0.27)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Layer</th>
<th>Ba-terminated surface</th>
<th>CeO-terminated surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>Ba(-0.47)</td>
<td>CeO Ce(-0.10) O(0.30)</td>
</tr>
<tr>
<td>O2</td>
<td>O(0.18)</td>
<td>O2 O(-0.04)</td>
</tr>
<tr>
<td>BaCeO</td>
<td>Ba(0.06) Ce(0.06) O(0.06)</td>
<td>O2 Ba(-0.13) Ce(0.06) O(-0.32)</td>
</tr>
<tr>
<td>O2</td>
<td>O(0.02)</td>
<td>O2 O(0.05)</td>
</tr>
</tbody>
</table>
Table 5.5 Average atomic displacements of atoms at BaCeO₃ surfaces. The average atomic displacement (Å) that occurred perpendicular to the surface was calculated in the four relaxed layers of the (001), (110), and (111) BaCeO₃ surface facets. For each surface, the initial and final coordinates for every atom in the relaxed layer were compared to examine how the layers relaxed perpendicular to the BaCeO₃ surface.

Upon summing the cleavage and relaxation energies of each of the different surface terminations, our results show that the (001) BaO-terminated surface is the most stable surface of the orthorhombic BaCeO₃ perovskite, though the (001) CeO₂ surface is also highly stable. Owing to immense surface relaxations, several (110) and (111) surfaces experience surface energies very close to the non-polar (001) surfaces. According to the data from this study, the stability of orthorhombic BaCeO₃ trends from most stable to least stable as: BaO(001), CeO₂(001), O(110), Ba(110), BaO₂(111), Ce₀.₅(111), O(111), CeO(110), O₂(110), BaO₂(111), Ce(111), BaCeO(110).
In nearly all cases, the non-stoichiometric surfaces of the polar (110) and (111) facets are more stable than their stoichiometric counterparts, as evidenced by lower cleavage energies and greater surface relaxations. These results are consistent with those found in SrTiO$_3$, BaTiO$_3$, and PbTiO$_3$ surface studies. This finding provides evidence that the reconfiguration of the polar surfaces of BaCeO$_3$ is a more adequate form of polarity compensation than a redistribution of electrons in the stoichiometric terminations.

5.4 Conclusion

The results of this study reveal that the (001) surfaces of orthorhombic BaCeO$_3$ are the most stable of those surfaces probed, owing predominately to their low cleavage energies. This finding would suggest that the (001) facet is the most common interfacial surface exposed on a grain of BaCeO$_3$. Comparably, a similar computational approach was used to determine that the (001) termination is the most stable for SrTiO$_3$. An experimental study conducted by Syha et. al using X-ray diffraction contrast tomography revealed that a single grain of sintered SrTiO$_3$ displayed a preference for the (001) interface, further supporting the computational findings. With this data we conclude that the (001) facet is the most energetically favorable surface facet of BaCeO$_3$ and will thus conduct all future perovskite interfacial studies on the (001) surfaces.

5.5 References


CHAPTER VI

COMPUTATIONAL INVESTIGATION OF DEFECT SEGREGATION AT THE (001) SURFACE OF BaCeO$_3$ AND BaZrO$_3$: THE ROLE OF METAL-OXYGEN BOND STRENGTH IN CONTROLLING VACANCY SEGREGATION

As published in *Journal of Materials Chemistry A*, 1, 2840-2846 (2013)

**6.1 Introduction**

Perovskite-type oxides have been widely studied for their high temperature proton conduction capabilities; interest now extends towards employing these ceramic materials for intermediate temperature (200-400°C) applications as well$^{1-3}$ While bulk conductivity remains higher than alternative solid electrolyte materials at these operating temperatures, recent work has identified that sluggish grain boundary (GB) conductivities in perovskites greatly reduce the overall conduction of protons at intermediate and lower temperatures$^{4-7}$ Much research has focused on identifying the origin of high resistance at perovskite grain boundaries in an effort to mitigate this detrimental phenomenon.

Early theories hypothesized that the reduction in GB conductivity originates from higher activation energies for proton transport due to structural variations in the interfacial region$^{1,8}$ However, recently it has been proposed that the development of a positive GB core charge repels protons away from the grain interface, reducing proton concentration and, consequentially, proton conductivity$^{5,9-11}$ The evolution of this core charge occurs from the segregation of
charged defects, namely positively charged oxygen vacancies, to the near interfacial area, within about 5-10Å from the crystalline surface.12,13

While numerous experimental results have provided indirect evidence that a positive GB core charge is responsible for the low GB conductivities in perovskites,5,6,9,13 new techniques have recently been employed to directly probe interfacial defect segregation to better understand the origin of the core charge. Maier et al. utilized a combination of transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDXS) to investigate dopant segregation in BaZrO3.14 They observed that dopant size did not contribute significantly to the segregation of the ions to the GB core, which suggests that elastic strain due to structural variations in the interfacial region does not constitute a major segregation driving force. Instead they attributed the segregation of dopants to an electrostatic interaction between the positively-charged GB core and the relatively negatively-charged dopant ions. A recent density functional theory (DFT) study of oxygen vacancy segregation at a BaZrO3 tilt GB revealed that the favorable formation energy of an oxygen vacancy (VO) in the first subsurface layer of the crystal may lead to the development of an electrostatic potential barrier similar to those seen in experimental studies.15 The researchers suggested this VO segregation occurs due to an electrostatic repulsion of oxygen ions between the two crystalline surfaces.

While these experimental and computational studies have offered insight into defect segregation at perovskite grain boundaries, the complex electrostatic interactions that occur in these material systems make it difficult to determine the fundamental factors that dictate interfacial defect segregation, and therefore to design improved materials on a rational basis. In the present work, we employ DFT to investigate dopant ion and oxygen vacancy segregation at a simple perovskite-vacuum interface in order to identify how intrinsic material and surface
properties influence defect segregation in the near interfacial region. By comparing segregation trends between BaZrO$_3$, which demonstrates relatively low GB conductivities,\textsuperscript{5} and BaCeO$_3$, which exhibits relatively high conduction across the GB region,\textsuperscript{16} we hope to gain an understanding of why disparate GB core charges develop in different perovskite materials.

6.2 Computational Methods

All DFT calculations were carried out using the plane-wave pseudopotential method as implemented by the Vienna Ab-Initio Simulation Package (VASP).\textsuperscript{17-20} For this study plane waves with an energy cutoff of 520 eV were constructed using projector augmented wave (PAW) potentials.\textsuperscript{21} The generalized gradient approximation (GGA) was applied using the PW91 exchange correlation functional. A 6 x 6 x 1 Monkhorst-Pack sampling of the Brillouin zone was utilized for all surface calculations, while a 6 x 6 x 6 k-point mesh was employed for bulk calculations.\textsuperscript{22}

The segregation studies were carried out at the two stoichiometric perovskite surfaces of the non-polar (001) surface facet. For BaCeO$_3$ this correlates to the BaO and CeO$_2$ terminated surfaces, while the BaO and ZrO$_2$ surfaces were examined for BaZrO$_3$. These surfaces were chosen because DFT studies have revealed that the (001)-terminated surfaces are the most stable for both of these perovskite materials.\textsuperscript{23,24} Furthermore, a recent experimental study using X-ray diffraction contrast tomography found that the (001) facet was the most prevalent termination in a single grain of SrTiO$_3$, a material whose DFT surface stability results trended similarly to those of BaCeO$_3$ and BaZrO$_3$.\textsuperscript{25}

In designing the unit cells for each of the segregation studies, we first geometrically optimized the ideal bulk structure of orthorhombic BaCeO$_3$ and cubic BaZrO$_3$ using a supercell consisting of 4 chemical formula units. The lattice constants obtained computationally for
BaCeO$_3$ were $a/\sqrt{2} = 4.50$ Å, $b/\sqrt{2} = 4.48$ Å, and $c/\sqrt{2} = 4.47$ Å, which are slightly larger than the experimental values of $a/\sqrt{2} = 4.41$ Å, $b/\sqrt{2} = 4.40$ Å, and $c/\sqrt{2} = 4.39$ Å. The computationally derived lattice constant for BaZrO$_3$ was calculated as $a = 4.19$ Å, while the value obtained experimentally was $a = 4.25$ Å. Geometric optimization resulted in lattice constants deviating less that 2% from experimental values for both perovskite materials.

The surfaces were modeled using a symmetrical 15-layered slab with the geometrically optimized bulk lattices. The symmetrical slabs were employed to cancel out any dipole moments that may develop, and a vacuum gap of 10 Å was introduced between each slab to mitigate any spurious interactions between cells. An optimization of vacuum gap thickness was completed and revealed that an increase in width from 10 Å to 11 Å yielded a change in material energy of less than 0.01%. The bottom eight layers of the slab were fixed to imitate the crystalline bulk and the defects of interest for each study were located in the top relaxed layers of the slab. This configuration allowed any energetic changes to be attributed to variations in defect arrangement at the top surface. Figure 6.1a and 6.1b depicts the BaO- and CeO$_2$/ZrO$_2$- terminated symmetric slab supercells used for the surface segregation study. The layers have been numbered from the relaxed top surface (layer 1) to the fixed bottom (layer 15).
Figure 6.1 Slab configurations of BaCeO<sub>3</sub> and BaZrO<sub>3</sub> (001) surfaces. 15 layer supercell slabs were employed for the segregation studies at the a) BaO surface and b) CeO<sub>2</sub>/ZrO<sub>2</sub> surface. Red denotes oxygen ions, green represents barium ions, and beige designates cerium or zirconium ions. Layers 8-15 were fixed to represent the bulk while layers 1-7 were allowed to relax. The ★ symbol denotes the location of the fixed yttrium dopant used for all segregation trials.

For each trial, two yttrium ions and one oxygen vacancy were introduced into each supercell to maintain overall electroneutrality. Yttrium dopants were substituted in the Ce and Zr lattice sites in BaCeO<sub>3</sub> and BaZrO<sub>3</sub>, respectively. Surface segregation was explored by systematically positioning the defects throughout the near surface environment. While dopant
ions and oxygen vacancies are considered mobile throughout this study, it is important to note that these defects have relatively high activation energies for diffusion compared to protonic defects. While oxygen vacancies are able to migrate at intermediate temperature ranges, dopant ions are generally considered immobile at temperatures below 1500°C. It is still important, however, to probe dopant configurations because sintering temperatures above 1500°C are typically reached during material synthesis, which allows the dopant ions to migrate and settle into their lowest energy configurations. Thus, our simulations are intended to capture the fact that dopant segregation can occur during high-temperature material processing, and that these dopant positions are then “frozen in” and may dictate how oxygen vacancies and protonic defects segregate during subsequent operation at low and intermediate temperatures.

Since complex Y-Y and Y-V$_O$ interactions are expected due to both coulombic and steric effects, the simulations were designed to control for compounding defect interactions. We began with a thorough investigation of defect segregation at the BaCeO$_3$ surface. One yttrium dopant was fixed in the bottom layer of the slab (denoted by the ★ symbol in Figure 6.1), while the second dopant was placed in various layers in the near surface environment. For each dopant configuration, the oxygen vacancy was placed systematically throughout the unit cell to discern how vacancy stability at the surface and near interfacial region varies with Y location.

We then explored how dopant atoms and oxygen vacancies segregate independently from each other in the BaCeO$_3$ and BaZrO$_3$ materials. To probe dopant segregation, one dopant ion and the oxygen vacancy were fixed in the bottom of the slab, while the second dopant ion was systematically positioned throughout the top, relaxed layers of the cell. Likewise, both the yttrium dopants were fixed in the representative bulk layers and the oxygen vacancy was placed throughout the near surface region of the relaxed interface to examine oxygen vacancy
segregation. Finally, we investigated how a coordinated Y-V\(_O\) pair segregates near the different perovskite surfaces by placing one yttrium dopant in the fixed bulk and varying the location of the pair in the near surface environment.

6.3 Results

6.3.1 BaCeO\(_3\) Study

We began with a detailed study of dopant ion and oxygen vacancy segregation at the BaCeO\(_3\) surfaces to determine the most favorable positions of the two defects relative to each other, as described in detail above. The study yielded two notable findings. First, in both surface environments the most stable configurations occurred when the Y and V\(_O\) were coordinated in nearest-neighbor sites. The formation of dopant-oxygen vacancy pairs is a common phenomenon that occurs between dopants and their charge compensating defects. This association has been studied in detail for a number of perovskites, including BaZrO\(_3\) and LaGaO\(_3\), and has been found to greatly impact the mobility of oxygen vacancies throughout the material, particularly at low temperatures.\(^{28-30}\)

While dopant-V\(_O^-\) pairs have been studied within bulk perovskites, to our knowledge this interaction has not been investigated at the perovskite surface. Our analysis shows that the position of the V\(_O^-\) relative to the surface impacts the stability of the Y-V\(_O^-\) pair. Figure 6.2 depicts how the material energy varies when the Y-V\(_O^-\) pair lies in the same horizontal plane and when the V\(_O^-\) is located in the neighboring site vertically below the dopant atom. For both the BaO- and CeO\(_2-\) terminated surfaces, the Y-V\(_O^-\) pair is most stable in the horizontal arrangement parallel to the surface. While the energy difference between the two configurations is only 10 kJ/mol (0.1 eV) at the BaO surface, the CeO\(_2\) surface shows a dramatic 100 kJ/mol (1 eV) difference in energy between the two positions.
Figure 6.2 Y-V° pair segregation at the BaCeO₃ (001) surfaces. Computational results comparing the orientation of the Y-V° pair in a horizontal arrangement (☐) parallel to the surface and a vertical arrangement (○) with the oxygen vacancy below the yttrium dopant at a) a BaO surface and b) a CeO₂ surface.

6.3.2. BaCeO₃ and BaZrO₃ Segregation Study

The results of the initial BaCeO₃ study suggested that the Y-V° pair positioned parallel to the surface is the most favorable configuration when the two defects are both mobile within the lattice. Based on this finding, we first decided to compare defect segregation of the two defects independently to access how the yttrium dopants and oxygen vacancies segregate at the two
different surfaces of both the BaCeO$_3$ and BaZrO$_3$ perovskites. We then completed a segregation study of the Y-V$_O$ pair in the favorable horizontal position to identify how segregation trends change when the defects are allowed to interact.

As no differences exist in the basic structure of the BaO surface between the BaCeO$_3$ and BaZrO$_3$ perovskites, it was hypothesized that little variation in defect segregation trends at this interface would be observed for these two materials. DFT calculations revealed that yttrium dopants were unstable in the first subsurface layer of the BaO surface for both perovskites (Figure 6.3a). On the other hand, oxygen vacancies were more stable by about 1eV at the top surface layer for both BaCeO$_3$ and BaZrO$_3$ (Figure 6.3b). Figure 6.3c depicts the segregation of the Y-Vo pair at the BaO surface of these two perovskites. The results indicate a slight stabilization when the V$_O$ is located at the BaO surface directly above the yttrium ion. However, the pair appears to be most favorable when positioned in a horizontal orientation toward the grain interior. These results indicate a tradeoff between favorable oxygen vacancy arrangement at the BaO surface and increased stability of Y dopants away from the interface.
Figure 6.3 Defect segregation at the (001) BaO surfaces of BaCeO$_3$ and BaZrO$_3$. Material energies for various defect segregation at the BaO surface of BaCeO$_3$ (□) and BaZrO$_3$ (♦). Energies presented as relative energy to the most favorable configuration for each surface. a) Yttrium dopant segregation b) Oxygen vacancy segregation c) Y-$V_O$ pair segregation

While segregation trends at the BaO surface appeared to be similar for the BaZrO$_3$ and BaCeO$_3$ perovskites, defect segregation trends diverge between the compositionally disparate CeO$_2$ and ZrO$_2$ surfaces. First, the data revealed that the yttrium dopant is stable at the ZrO$_2$ interface, whereas the dopant ion is destabilized at the CeO$_2$ surface (Figure 6.4a). Next, the DFT results suggested a stabilization of oxygen vacancies in the first subsurface layer of ZrO$_2$. At the CeO$_2$ surface, however, oxygen vacancies were found to be more unstable in this first subsurface
layer (Figure 6.4b). Finally, the Y-V\textsubscript{O} pair segregation study revealed an energetic stabilization of 0.7eV when the Y-V\textsubscript{O} pair was located at the ZrO\textsubscript{2} surface. The reverse trend was found for the CeO\textsubscript{2} surface, where the Y-V\textsubscript{O} pair tended to segregate away from the interfacial region (Figure 6.4c).
Figure 6.4 Defect segregation at the (001) CeO$_2$ surface of BaCeO$_3$ and the (001) ZrO$_2$ surface of BaZrO$_3$. Material energies for defect segregation at the CeO$_2$ and ZrO$_2$ surfaces of BaCeO$_3$ (□) and BaZrO$_3$ (♦), respectively. Energies presented as relative energy to the most favorable configuration for each surface. a) Yttrium dopant segregation b) Oxygen vacancy segregation c) Y-V$_O$ pair segregation

6.4 Discussion

The results of these DFT studies provide insights into the complex factors that may influence the development of a grain boundary core charge within perovskite materials. At the BaO surface, the V$_O$ segregation study suggests that the singly coordinated oxygen ion at the perovskite surface is unstable, as evidenced by the favorable configuration of the oxygen vacancy at the top surface layer. This finding might indicate an increased likelihood for a positive grain boundary core charge to develop at this interface, as the +2 charged oxygen vacancies preferentially segregate to the surface. However, it is also necessary to consider the dopant segregation in the interfacial environment. Since the oxygen ion at the surface experiences a reduction in coordination, it is more favorable for the unstable oxygen to be bonded with a higher valence cation that can donate more electrons. Therefore, the +3 yttrium cation is unstable near the BaO surface. This trend becomes important when exploring the Y-V$_O$
pair segregation that occurs near the interfacial region. When the defects are able to interact as a Y-V\_O pair, they tend to segregate away from the BaO surface. This result suggests that the favorability of the Y dopant to be located away from the interface dominates the pair segregation and potentially destabilizes the V\_O at the surface, reducing the probability that a positive interfacial charge will develop.

The segregation driving forces are distinctly different at the chemically unique CeO\_2 and ZrO\_2 surfaces. At these interfaces the oxygen coordination of the surface cation species, either Ce, Zr, or Y, is reduced from six to five. We thus hypothesized that for each perovskite material, the cation species with a stronger oxygen bond strength would be more stable away from the material surface where oxygen coordination is maximized. We calculated the M-O bond strength (where M=Ce, Zr, Y) by first calculating the energy of a unit cell of stoichiometric BaCeO\_3 and BaZrO\_3, as well as unit cells of BaCeO\_3 and BaZrO\_3 each with one yttrium atom substituted into it. Next, one Ce, Zr, or Y was removed from the cell and the energy was recalculated. The bond strength was defined as:

\[
E_{M-O} = \frac{1}{6}[E_{\text{original cell}} - E_{M\text{ removed}} - E_M]
\]

(6.1)

where \(E_M\) is the energy of a single metal atom and 1/6 is applied because there are six oxygen bonds formed with each M atom.

The results of our bond strength calculations indicated that in BaZrO\_3 the Zr-O bond is about 70 kJ/mol (0.7 eV) stronger than the Y-O bond. This suggests that the material energy should be about 70 kJ/mol (0.7 eV) lower when the yttrium dopant is located at the material surface, maximizing the number Zr-O bonds throughout the material. Indeed our DFT results show that it is about 70 kJ/mol (0.7 eV) more favorable for the yttrium dopant to segregate to the surface rather than allowing the Zr ions to populate the interfacial layer. In contrast, the Y-O
bond is about 20 kJ/mol (0.2 eV) stronger than the Ce-O bond within the BaCeO$_3$ material. This suggests that increasing the Y-O coordination would minimize the material energy. Our DFT results support this hypothesis, since the energy minimization that occurs when the yttrium dopants segregate away for the CeO$_2$ surface is about 40 kJ/mol (0.4 eV), which is slightly larger than expected based on the bond strength calculations.

The results from these findings indicate that inherent material properties may influence the enthalpic driving force for dopant segregation to perovskite surfaces. Recent experimental findings suggest that relatively negatively charged dopant atoms migrate to the grain boundary region because of a coulombic attraction with the positive grain boundary core. However, this study reveals that the interaction of the dopant species with the host perovskite material may lead to an increased favorability of dopant segregation to the perovskite interface despite the absence of a grain boundary core charge.

As shown in the DFT results, oxygen vacancy segregation trends at the CeO$_2$ and ZrO$_2$ surfaces are also in contrast: vacancies are stabilized in the first subsurface layer of the ZrO$_2$-terminated material but are destabilized in the first subsurface layer of the CeO$_2$-terminated material. These contrasting trends suggest that a difference in surface properties likely influences the segregation of the oxygen vacancies at these perovskite surfaces. A recent computational study of oxygen vacancy segregation at a BaZrO$_3$ tilt grain boundary resulted in a similar finding of $V_O^-$ stabilization in the first subsurface layer from the grain boundary interface. While that study suggested that the stabilization stems from oxygen ion repulsion that arises from the grain-grain interactions, the comparable finding from this simplified perovskite-vacuum interfacial study supports the notion that inherent material properties combined with structural variations in
the grain boundary region may influence oxygen vacancy segregation in the near surface environment.

The results from the $Y-V_O^-$ pair segregation study at the CeO$_2$/ZrO$_2$ surfaces indicate a similar finding as the BaO interfacial study. These data suggest that dopant location may influence the stability of oxygen vacancies at the perovskite surface through the $Y-V_O^-$ pair interaction. The Y dopant and oxygen vacancy both were found to be stable at the ZrO$_2$ surface, which may contribute to the highly favorable $Y-V_O^-$ pair segregation to this interface as reported from the DFT results. Likewise, the instability of the Y dopant at the CeO$_2$ surface may have contributed to the favorable segregation of the $Y-V_O^-$ pairs away from this interface.

By comparing the segregation trends of both defects independently from one another and then synergistically we have gained potential insight into designing perovskite materials that may mitigate the development of a positive grain boundary core charge. The results of these studies suggest that the configuration of the yttrium dopants may act to stabilize or destabilize oxygen vacancies in the near interfacial environment. At the BaO surface, oxygen vacancies were stable in the top surface layer in the absence of the dopant ions. However, the instability of the yttrium dopants at the surface appears to destabilize this arrangement when the defects are allowed to interact. The DFT results revealed that the yttrium dopants were favorably positioned at the ZrO$_2$ surface. This may have increased the stability of the oxygen vacancy at this interface by stabilizing the $Y-V_O^-$ pair at the surface. In contrast, the yttrium dopants were unstable at the CeO$_2$ surface, potentially reducing the stability of the $Y-V_O^-$ pair at the surface.

These results suggest that designing perovskites where the dopant ions are unstable at the material interface may mitigate the development of a positive grain boundary core charge through a reduction of $Y-V_O^-$ pairs at the surface. For example, by screening for materials with
higher dopant-oxygen bond strengths compared to the bond strength of the host tetravalent cations and oxygen anions, it may be possible to identify perovskites that have a reduced enthalpic driving force for dopant ions to segregate to the material interfaces. This would in turn decrease the stabilization of oxygen vacancies in the surface through reduced dopant-V\text{O} pair segregation to the material interface, thus decreasing the development of the positive grain boundary core charge.

A number of potential dopant ions, including In, Ga, Yb, and Sc, were screened to identify dopants that may enhance grain boundary conductivity in BaZrO\textsubscript{3}. A bond strength analysis revealed that Sc has an oxygen bond strength of -250 kJ/mol (-2.6 eV) within the BaZrO\textsubscript{3} perovskite, which is about 10 kJ/mol (0.1 eV) stronger than the Y-O bond strength of -240 kJ/mol (-2.5 eV). The other screened dopants exhibit oxygen bond strengths less than that of Y-O. These results may indicate that Sc ions are less likely to segregate to the BaZrO\textsubscript{3} surface. Shirpour \textit{et al} compared the segregation of Sc and Y to the BaZrO\textsubscript{3} grain boundaries and found that Sc exhibits a lower degree of segregation to these interfacial regions than Y\textsuperscript{14}. While this difference may be caused by the difference in size between the dopant ion and host cation (Y has a 0.2 Å larger ionic radius than Zr, while Sc is comparable in size to Zr), the difference between the enthalpic driving forces for surface segregation may also play a role in the disparate segregation trends. The study also revealed that the Sc-doped BaZrO\textsubscript{3} exhibits higher grain boundary conductivities than the Y-doped samples in nearly all conditions tested. This result may provide evidence that strong dopant-oxygen bond strengths may contribute to higher grain boundary conductivities through reduced dopant segregation to the perovskite interface.
6.5 Conclusion

In this study, yttrium dopant and oxygen vacancy segregation was studied at the BaO and CeO$_2$/ZrO$_2$ surfaces of BaCeO$_3$ and BaZrO$_3$. Defect segregation was assessed independently and then synergistically to gain insight into how intrinsic material properties may drive defect segregation in perovskite-type materials. The results suggest that the dopant ion position may act to stabilize or destabilize oxygen vacancies near the material surface. At the BaO surface of both perovskite materials, the oxygen vacancy was found to be more stable when not in the presence of the dopant ion. However, when the dopant interaction was included, the Y-V$_O$ pair was unstable near the BaO surface, trending similarly to the independent yttrium segregation. At the ZrO$_2$ surface both the Y dopants and oxygen vacancies were independently stable at the BaZrO$_3$ interface. When the defects were allowed to interact as a pair, the defects were further stabilized at the surface. The opposite phenomenon occurred at the CeO$_2$ surface, where the Y, V$_O$ and Y-V$_O$ pair were all unstable near the BaCeO$_3$ interface. These results suggest that by designing perovskites such that the dopant ions are unfavorably located at the material surface, there may be a destabilization of the positively charged oxygen vacancies at the interface and a subsequent decrease in the likelihood of a positive grain boundary core charge to develop.

6.6 References

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CHAPTER VII

AN AB-INITIO INVESTIGATION OF PROTON STABILITY
AT BaZrO₃ INTERFACES

7.1 Introduction

Protons encounter several varieties of interfaces within a perovskite system, such as the grain boundary (GB) during proton conduction,¹⁻⁴ the material surface during catalysis,⁵⁻⁷ and the triple phase boundary (TPB) within electrochemical devices.⁸⁻¹⁰ Proton chemistry at and near these regions greatly influences the behavior of devices for which these perovskites are being implemented; yet many questions remain about the proton behavior within these complex environments. For example, it is well known that proton conductivity in many perovskites, such as BaZrO₃, is orders of magnitudes lower across the grain boundary (GB) interfaces than within the material bulk.¹¹ While sluggish proton conduction across this region limits overall perovskite conductivity, there is still only limited understanding of proton stability and mobility at the GB interfaces.¹²⁻¹⁴ Additionally, recent evidence shows reasonable catalytic activity for the oxygen reduction reaction in many proton conducting perovskites, but it remains unclear how the surface protons and electronic structure influence catalytic behavior.¹⁵⁻¹⁷ Finally, little work has been done to assess proton chemistry at the TPB, despite its importance to the performance of electrochemical devices, such as proton conducting ceramic fuel cells and electrolyzers. The
importance of and dearth of knowledge about proton chemistry at perovskite interfaces motivates further atomistic level studies of these interfacial environments.

While few studies have yielded a fundamental understanding of proton chemistry at perovskite interfaces, experimental and computational studies have provided important insights into general proton behavior. For example, recent impedance spectroscopy studies have revealed that GB conductivities within perovskite oxides can be as much as two orders of magnitude lower than the bulk conductivity, limiting the material’s overall conduction capabilities and reducing its commercial viability.\(^{11,18}\) The source of reduced GB conduction in perovskite materials, particularly in the promising BaZrO\(_3\), has been examined both experimentally\(^{2,12}\) and computationally.\(^{13,19-21}\) Recent evidence suggests that a positively charged GB core develops as a result of defect segregation to the GB interface. The core charge leads to a space charge effect, such that protons are repelled away from the positively charged barrier, decreasing proton conduction across the GB interface.\(^{14,22,23}\) While the existence of this interfacial charge is detrimental to overall material conductivity, little evidence exists to explain the origin of the positive GB core charge or how the protons behave near the GB region.\(^{13,19}\)

Attention has long been focused on the promising conduction capabilities of perovskite oxides; yet recent studies of the material have broadened to explore the viability of perovskites as catalysts within electrochemical devices to replace expensive precious metals. While numerous studies have shown promising activity for the oxygen reduction reaction (ORR) on various perovskite surfaces,\(^ {6,24}\) the complexity of both the reaction and the perovskite material has made it difficult to identify the rate limiting step of this electrochemical reaction.\(^ {15}\) With limited knowledge about the fundamental reaction mechanism, the ability to design enhanced catalytic surfaces using first principle techniques remains elusive. Work now focuses on trying
to understand how perovskite structural and electronic properties influence and enhance ORR activity. Suntivich et al. identified an optimal filling of the transition metal $\sigma^*$ orbital in the bulk that maximizes ORR activity. Additionally, Lee et al. established a descriptor for ORR activity using the bulk oxygen p-band center. These studies have begun to reveal important parameters that influence the catalytic properties of perovskites, yet they still rely only on bulk material properties and lack details on the role proton surface chemistry plays on the ORR activity. Since the protons are active participants in the ORR, their mobility and concentration at and near the surface likely contributes to the catalytic activity of most, if not all, perovskite surfaces. Furthermore, according to Sabatier’s principle, proton adsorption strength on the perovskite surface should also play a role in catalyst activity. Thus, investigation of proton chemistry at the perovskite surface must be completed to aid the design of more effective ORR catalysts.

Despite interest in replacing precious metal catalysts with perovskite materials, traditional electrochemical devices, such as solid oxide fuel cells (SOFCs), rely on these metals for sufficient performance. The incorporation of the metal electrode causes the formation of three phase interfacial regions between the electrode, electrolyte, and the gaseous reactants, known as the triple phase boundary (TPB). In SOFCs with proton conducting electrolytes, such as perovskites like BaZrO$_3$, protons generated at the anode travel through the electrolyte and contribute to the formation of water on the cathode electrode. The reactions at the TPBs and the conduction of protons into and out of the electrolyte in the near TPB environments play a critical role in fuel cell performance. However, the complex heterointerface has made it difficult to probe proton behavior near the TPB interface. Therefore, rudimentary studies of proton chemistry in the TPB region could begin to shed light on how this complicated interface affects proton stability within the electrolyte.
The goal of this study is to use density functional theory (DFT) to gain an atomistic level understanding of proton behavior at BaZrO$_3$ interfaces to identify opportunities and strategies to design and screen for perovskites with enhanced functionality. First, we present an analysis of proton stability in the near surface environments of the (001) BaO- and ZrO$_2$- vacuum interfaces. An examination of the density of states of the oxygen atoms in this interfacial region provides evidence to explain stability trends of protonic defects in layers near the perovskite surface. We show that changes in the oxygen p-band center greatly influence the stability of protons at the surface and in the near interfacial region. To verify these results we then test the p-band center hydration predictor model within bulk yttrium-doped barium cerate.

Finally, we assess how the introduction of metal nanoclusters to the perovskite surface changes proton stability in the near-heterointerfacial region of BaZrO$_3$ as a model of the triple-phase boundary. Palladium, platinum, nickel, and silver clusters are arranged at the two (001) surfaces to form BaZrO$_3$-metal interfaces. A comparison of proton stability between the BaZrO$_3$-vacuum and BaZrO$_3$-metal interfaces indicates that the incorporation of all of the metals tested increases proton stability in the first several layers of the perovskite-metal heterointerface. Applying the p-band center model developed in the first part of this study, we find that the p-band center is not an accurate predictor for proton stabilization at the perovskite-metal heterointerface as additional factors, such as proton bonding with adjacent metal atoms, influence the adsorption energy.

7.2 Computational Methods

All DFT calculations were carried out using the Vienna Ab-Initio Simulation Package (VASP).$^{29-32}$ Plane waves with an energy cutoff of 500 eV were constructed using projector augmented wave (PAW) potentials.$^{33}$ The generalized gradient approximation (GGA) was
applied using the PW91 exchange correlation functional. A $2 \times 2 \times 1$ Monkhorst-Pack sampling of the Brillouin zone was utilized for all surface calculations.$^{34}$ A $4 \times 4$ BaZrO$_3$ unit cell was used throughout.

The proton stability studies at the BaZrO$_3$-vacuum interface were conducted on a 19 layer symmetrical slab at both the BaO and ZrO$_2$ (001) surface terminations. The (001) surfaces were chosen because they have been determined to be the most stable surface terminations of BaZrO$_3$.\textsuperscript{35,36} The thickness of the slab was set at approximately double the width of the space charge layer, $d_{\text{space charge}} \sim 20\text{Å}$, so that any (de)stabilizing effects from the opposite surface did not interfere with the stability study. The bottom 10 layers of the slab were fixed to simulate the perovskite bulk, while top 9 layers were allowed to relax. A vacuum gap of 10 Å was included to prevent any spurious effect between cells.

To maintain electroneutrality, each hydrated unit cell contained two yttrium ions and two protons. Both dopant atoms and one proton were arranged in the bottom, fixed layers of the cell, far enough away from the top layers to avoid any interactions with the proton of interest. The locations of these three defects were fixed for the unhydrated case as well, so any variation in adsorption energy could be attributed solely to the upper proton. The location of the upper proton was varied throughout the top, relaxed layers of the slab model to probe how proton stability varied in the near-surface environment. (When a proton is referred to in the remainder of this chapter, it refers to this upper proton).

Proton stability was assessed by calculating the proton adsorption energies for a number of configurations:

$$\Delta E_{\text{adsorption}}^i = E_{\text{hydrated}}^i - E_{\text{control}} - E_H$$

(7.1)
where $E_{hydrated}^i$ denotes the energy of the cell hydrated in layer $i$ from the surface, $E_{control}$ represents the energy of the cell without the proton of interest, and $E_H$ is the energy of a single hydrogen atom. The proton was configured 1 Å away from an oxygen atom to model OH bonding. The protons were bonded to oxygen ions at different depths from the perovskite surface, varying from surface oxygen ($i=1$) to bulk oxygen ($i=8$) (refer to Figure 7.1a and 7.1b). The orientation of the proton with respect to the perovskite surface was also considered by configuring the proton in various positions with respect to the material surface. In the layers where the proton is able to rotate perpendicularly to the cell surface, the proton was oriented at an upward, side, or downward configuration to see if orientation influenced proton stability (Figure 7.1c). In the layers where the proton is able to rotate parallel to the material surface, the proton was oriented pointing toward one of its 4 next nearest neighbor oxygen ions.

![Figure 7.1 Atomic configurations of the (001) BaZrO$_3$ surfaces.](image)

Surface structures of the (a) BaO and (b) ZrO$_2$ termination constructed of oxygen (red), barium (green) and zirconium (beige) ions. The circled oxygen ions indicate those oxygens with which the protons were bonded to during the proton stability studies. The tested proton configurations are depicted in (c). When the
proton is able to rotate perpendicularly to the surface, the proton is oriented upward, sideways, and downward with respect to the perovskite surface. When the proton may rotate parallel to the surface it is oriented sideways with respect to the surface pointing toward a next nearest oxygen neighbor.

An electronic density of states (DOS) analysis was conducted to probe the origins of the proton stability trends revealed from this hydration study. In DFT the DOS is calculated as the number of electrons with energies between E and E+dE. An important parameter to describe the DOS is the center of the valence band, which denotes the weighted average of the electrons within the band. As we are probing how the electron distribution within oxygen atoms influences hydration of the oxygens, we calculated the p-band centers of the oxygens with which the protons were bonded. All p-band centers were referenced to the Fermi energy, $\varepsilon_F$. The $\varepsilon_F$ represents the highest energy level that electrons may occupy. As the p-band center shifts closer to $\varepsilon_F$, more electrons become available for binding. All DOS analyses were performed on unhydrated slabs to identify how the spread of electron distribution within oxygen atoms changes between different perovskite layers in the near-interfacial region.

Recent work has suggested that the bulk oxygen p-band center may be a useful predictor for sorption on perovskites.\textsuperscript{15} To determine whether a trend between p-band center and adsorption energy can be applied to different perovskite systems, we calculated the p-band center and adsorption energy for bulk yttrium-doped BaCeO$_3$, a system we have studied in detail previously.\textsuperscript{37} Three dopant concentrations were examined: 50%, 25%, and 12.5%. Unit cells were constructed such that two yttrium atoms were incorporated into each cell to obtain the desired dopant concentration. Therefore, the 50%-doped cell contained 4 chemical formula units of BaCeO$_3$, the 25%-doped cell included 8 chemical formula units, and the 12.5%-doped cell comprised 16 chemical formula units. The yttrium atoms were arranged in the most stable
configurations determined from bulk BaCeO$_3$ described in Chapter 4 of this thesis. The proton adsorption energies were calculated such that:

$$\Delta E_{\text{adsorption}} = E_{\text{BCY}+H} - E_{\text{BCY}} - E_H$$

(7.2)

$E_{\text{BCY}+H}$ denotes the cell with a single hydrogen atom, $E_{\text{BCY}}$ represent the BCY cell with no protons within it, and $E_H$ is the energy of a single hydrogen.

In the final part of this study, material hydration was probed at the BaZrO$_3$-metal heterointerface. Due to the increase in computational resources required to complete the BaZrO$_3$-metal interfacial simulations, the unit cells for these calculations were simplified. A smaller unit cell was constructed with 9 layers, such that the bottom 5 layers were fixed and the top 4 layers were allowed to relax. To simulate the complex BaZrO$_3$-metal heterointerface, a 10 atom metal cluster was optimized atop each of the two perovskite surfaces. A 10 atom cluster was chosen because it forms a stable particle (a cleaved section of a full shell “magic number” 13 cluster). The width of the 10 atom cluster was also advantageous because it could be arranged on the 4 x 4 BaZrO$_3$ unit cell such that there were gaps between neighboring metal clusters. This ensured that the minimum amount of perovskite lattice deformation occurred at the heterointerface. It is important to note that BaZrO$_3$-metal interfacial structure is currently unknown experimentally. While a 10 atom metal cluster does not likely represent the accurate 2D interface that occurs in vivo, it allows us to explore the effect of the metal interaction on the stability of protons in the environment directly under the metal cluster.

Four metals with varying electronic properties were investigated: platinum, palladium, silver, and nickel. First, the palladium metal clusters were geometrically optimized to provide a model for how to arrange the remaining metal atoms. This was done first by examining several
different initial configurations of Pd atoms on the two perovskite surfaces. Cluster stability was assessed by calculating the clustering energy:

$$E_{Cu}^{clus} = E_{Cu}^{clus} - E_{Cu}$$

(7.3)

where $E_{Cu}^{clus}$ denotes the total energy of the metal cluster on the perovskite surface, $E_{Cu}$ represents the energy of the bare perovskite slab, and n describes the number of metal atoms in the cluster. First, a layer of 7 Pd atoms was arranged on the two BaZrO$_3$ surfaces to optimize the bottom layer of metal atoms. It was noted that when the metal was allowed to relax the arrangements geometrically optimized to a more stable 5 atom bottom layer with 2 Pd atoms above. We thus probed two 10 atom cluster configurations: a 7/3 configuration (7 metal atoms on bottom, three on top) and a 5/4/1 configuration (5 atoms on bottom, 4 in the middle, 1 on top). Both schemes were tested, and the 5/4/1 arrangement proved to be the most energetically favorable on both surfaces. This 5/4/1 arrangement was then used to geometrically optimize the remaining 4 metal clusters to control for cluster configuration between the different BaZrO$_3$-metal heterointerfaces.

Protons were then arranged within the first three perovskite layers near the BaZrO$_3$-metal heterointerfaces, as well as in the same positions at an identical BaZrO$_3$-vacuum interface. This provided a direct comparison between the vacuum and metal interfaces to determine the effect of the metal on proton stability. Proton stability was assessed by comparing changes in the proton adsorption energies between the BaZrO$_3$-metal systems and the control, vacuum configurations:

$$\Delta E_{vacuum}^i = E_{BaZrO3+H}^i - E_{BaZrO3} - E_H$$

(7.4)

$$\Delta E_{metal}^i = E_{BaZrO3/metal+H}^i - E_{BaZrO3/metal} - E_H$$

(7.5)

$$\Delta E_{stability}^i = \Delta E_{metal}^i - \Delta E_{vacuum}^i$$

(7.6)
A positive value of $\Delta E_{\text{stability}}^{\ell_i}$ represents a reduction of proton stability in the $i$ layer as a result of the introduction of the metal clusters. A negative $\Delta E_{\text{stability}}^{\ell_i}$ value denotes that the introduction of the metal to the BaZrO$_3$ surface leads to an increase in proton stability in the $i$ layer.

7.3 Results and Discussion

7.3.1 Proton Stability at the BaZrO$_3$-Vacuum Interface

Figure 7.2 depicts the proton adsorption energies for the proton configurations at both the BaO and ZrO$_2$ perovskite-vacuum interfaces. A similar trend in proton stability occurs at both the (001) terminations. First, there is a significant stabilization, 50-100 kJ/mol (0.5-1 eV), that occurs when the proton is bonded to an oxygen at the perovskite surface. At the BaO surface, the orientation of the surface proton (whether the proton is pointed up away from the surface or to the side perpendicular to the surface) has no impact on the stability of the proton. A proton oriented in any direction at the BaO surface results in a negative adsorption energy, indicating that proton bonding is favorable at this layer. On the other hand, proton orientation does influence the stability of the proton at the ZrO$_2$ surface. The results indicate that the parallel proton experiences a favorable adsorption energy while the alternative orientations, up and down, experience positive, or unfavorable, adsorption energies. An analysis of the relaxed structure reveals that the sideways proton reorients to point slightly upward, suggesting that this is the more favorable proton configuration at the ZrO$_2$ surface.

As the proton is moved toward the perovskite bulk, it experiences a destabilizing effect when bonded to an oxygen atom in the first subsurface layer below both the BaO and ZrO$_2$ surfaces. This destabilization effect ranges from approximately 50-200 kJ/mol (0.5-2 eV), when compared to the surface adsorption enthalpies. Proton stability then increases slightly in the
second subsurface layer (Layer 3) and decreases slightly in Layer 4. After layer 4 the perturbation in proton stability subsides and adsorption energies becomes slightly more favorable as the proton is moved toward the crystalline bulk. Other than at the ZrO$_2$ surface, the data suggests that orientation plays a small role in the stability of the protonic defect.

(a)
Figure 7.2 Proton adsorption energies at the (001) BaZrO surfaces. Adsorption energy of protons bonded to oxygen ions various distances from the perovskite surface, ranging from surface oxygens (Layer 1) to bulk oxygens (Layer 8), near the (a) BaO interface and (b) ZrO$_2$ interface. Three proton orientations were tested throughout the cell: up toward the surface (☐), sideways parallel to the surface (○), and down away from the surface (△).

While the adsorption energy exhibits similar proton stability trends at both the BaO and ZrO$_2$ surfaces of BaZrO$_3$, the absolute values of the adsorption energy between the two surfaces differ greatly. Proton stability near the BaO surface is favorable, evidenced by the negative adsorption energy values, in all layers except for the second and fourth subsurface layer. The ZrO$_2$ surface, on the other hand, yields unfavorable adsorption energies in all layers but a single orientation at the surface. To understand proton stability variations in the near surface environment of the BaZrO$_3$ crystal, an analysis of the electron density of states was conducted on oxygen atoms at various depths within the slab. Specifically, the p-band structure was explored, as the s-band poorly describes the valence electrons available for bonding. As the p-band center, or the weighted average of the p-band, shifts toward the Fermi level, more electrons become
available for bonding. In general, an increase in the valence band center typically leads to a greater adsorption strength between the atom and its adsorbate.

Figure 7.3 depicts the p-band centers for each oxygen atom that was probed at both the BaO-vacuum and ZrO$_2$-vacuum interfaces. The results of the p-band analysis revealed a similar, yet opposite, fluctuation in the p-band centers compared to the adsorption energies displayed in Figure 7.2. That is, the surface oxygens yielded high p-band centers, followed by low p-band values for oxygens in the first subsurface layers, and then a slight increase in p-band centers before leveling out into consistent p-band values toward the material bulk.

Figure 7.3. P-band centers of oxygen ions at the (001) BaZrO$_3$ surfaces. Oxygen p-band centers at various distances from the (001) BaO (○) and ZrO$_2$ (□) perovskite surfaces.

Figure 7.4 depicts the relationship between p-band center and adsorption energy. Specifically, the p-band center for each oxygen is plotted against the average value of the adsorption energies for the protons bonded to the given oxygen. The resulting trend indicates that
adsorption energy decreases, or becomes more favorable, as the p-band center of the oxygen increases toward the Fermi level.

Figure 7.4 P-band center analysis at the (001) BaZrO₃ surfaces. P-band center vs. adsorption energy of oxygen atoms in the near interfacial environment of (001) BaO (○) and ZrO₂ (□) surfaces.

The results from this surface interfacial study have multiple implications. First, the instability of protons in the first subsurface layer could provide potential insight into the reduced grain boundary conductivities seen experimentally. Recent examination of the perovskite GB region has revealed that a positive grain boundary core charge likely forms within these materials, creating a space charge layer with a diminished proton concentration.

This study demonstrates proton instability in the first subsurface layer of the perovskite interface, creating a potential activation barrier for proton mobility to/from the surface. While the grain boundary interface is much more complex than the perovskite-vacuum surface, our previous studies have shown that studying the simplified perovskite surface can yield important fundamental trends that may also translate to the more complicated GB region. Here we see that proton conduction
in the GB interface may result from a combination between proton instability near perovskite interfaces as well as a positive grain boundary core charge determined from experiments.

Furthermore, these results demonstrate a distinct difference in proton stability between the perovskite surface and the material bulk, likely due to disparate electron distributions in the oxygen atoms in these two environments. Previous studies have shown a correlation between bulk oxygen p-band centers and ORR catalytic activity.\textsuperscript{15} We show here that bulk oxygen p-band centers are likely not the most accurate descriptors for catalytic activity because oxygen electronic properties vary at the perovskite surface. While it is more difficult to evaluate the surface oxygens of perovskite oxides because the surface structures are not precisely known, analyzing the most stable surfaces as determined by DFT may provide a more accurate descriptor of ORR activity.

Finally, the relationship between p-band center and proton adsorption energy discovered in this study provides a potentially significant model to screen for perovskites with enhanced hydration properties. The immensely large number of combinations of perovskite oxides and dopant atoms is expensive and time consuming to explore experimentally. This p-band center model establishes a simple parameter that can be computed \textit{in silico} to identify perovskite-dopant combinations that may exhibit enhanced hydration properties.

**7.3.2 P-Band Analysis within Bulk Yttrium-Doped Barium Cerate**

The linear correlation between oxygen p-band center and adsorption energy revealed in the BaZrO$_3$-vacuum interfacial study has potential implications toward understanding why hydration within perovskite oxides varies between systems. To substantiate this model, we carried out a similar DOS analysis on a different perovskite system: bulk yttrium-doped barium
cerate (BCY). The results of this study, depicted in Figure 7.5, reveal that the linear correlation between oxygen p-band center and adsorption energy found at the BaZrO\textsubscript{3} surface also exists within the BCY bulk.

**Figure 7.5 P-band center analysis within bulk yttrium-doped barium cerate (BCY).** P-band center vs. adsorption energy of oxygen atoms in 50\% (O), 25\% (□), and 12.5\% (∆) yttrium-doped barium cerate (BCY).

To gain a better understanding of the discrepancies in p-band center and adsorption energy within each of the BaCeO\textsubscript{3} systems, we first take a closer look at the 50\%-doped sample. Figure 7.6 depicts the unit cell and p-band center plot for 50\%-doped BCY. In this unit cell, every oxygen ion is bonded with one cerium and one yttrium ion, thus allowing for a structural analysis irrespective of yttrium coordination. While 50\%-doped BCY is not synthesized experimentally because A-site doping is limited to dopant concentrations less than about 25\%, this system is computationally convenient to study due to its small unit cell.\textsuperscript{1} Since BaCeO\textsubscript{3} is comprised of an orthorhombic crystalline lattice, there are variations between Ce-O bond lengths
in different axes of the system. The experimental lattice constants for BaCeO$_3$ are $A=8.78$ Å, $B=6.23$ Å, and $C=6.22$ Å, so the Ce-O (or Y-O) bond lengths along the vertical axis of the pictured unit cell are longer than the bond lengths along the horizontal axis. The p-band vs. adsorption energy plot in Figure 7.7 distinguishes between the two groups of oxygens, where the “vertical” oxygens are those that reside in the vertical O-Ce-O axis and the “horizontal” oxygens are those that exist in the horizontal O-Ce-O axis.

![Figure 7.6](image)

**Figure 7.6 Electronic analysis of proton stability within 50%-doped BCY.** (a) The unit cell of 50% yttrium-doped barium cerate (BCY50), comprised of oxygen (red), barium (green), cerium (beige), and yttrium (blue) ions. (b) P-band center vs. adsorption energy of oxygens within BCY50 configured along the vertical (○) and horizontal (□) axes.

The results indicate a discrepancy between the p-band centers of the horizontal and vertical oxygen atoms. The oxygens situated on the horizontal axes, where the Ce/Y-O bond lengths are shorter, have a p-band center shifted higher toward the Fermi level than those oxygens positioned on the vertical axes. The higher p-band centers appear to contribute to more favorable proton adsorption on the horizontal oxygen ions. This behavior has been discussed
previously. Kreuer suggests that the deviation from the cubic lattice structure within orthorhombic perovskites causes different binding energies between disparate lattice sites. These different binding sites lead to preferential proton diffusion in one direction with restricted mobility between different paths, leading to decreased proton mobility within the material.\textsuperscript{39,40} The results presented here provide clear electronic evidence to support this explanation.

A closer investigation of the BCY25 (25\% doped) results can provide further insight into how dopant coordination influences the electronic structure and hydration favorability of oxygen ions. Figure 7.7a depicts the BCY25 unit cell, where the two yttrium atoms have been substituted into two neighboring Ce ion lattice sites. This configuration results in two vertical oxygen ions bonded to the two yttrium dopant ions, while the remaining six vertical oxygens are coordinated with two cerium ions. Figure 7.7b displays the plot of p-band centers versus adsorption energies between each of the oxygen ions within the system. The results, confirmed through additional analysis, show the two oxygens that are coordinated only to the yttrium ions have the highest p-band centers as well as the most favorable adsorption energies within the system. The remaining vertical oxygen ions follow the same trend as in the BCY50 systems, showing lower p-band centers and less favorable adsorption energies compared to the horizontal oxygens.

The horizontal oxygens can also be assessed in relation to the yttrium dopants. Eight horizontal oxygen ions are bonded to one cerium and one yttrium ion, while the remaining eight are bonded only to cerium ions. The results show that the “horizontal” oxygens coordinated with the yttrium ion have slightly higher p-band centers, as well as more favorable adsorption energies, than those oxygens bonded only to cerium ions. It has long been theorized that yttrium dopants increase the basicity of the oxygen ions in the surrounding area, influencing the hydration favorability of those oxygens. The data presented here supports this hypothesis,
revealing that yttrium coordination shifts the oxygen’s electron distribution toward the Fermi level, causing the oxygen to become more basic. This increases the number of electrons available for binding, thus increasing the favorability of proton adsorption.

Figure 7.7 Electronic analysis of proton stability within 25%-doped BCY. (a) The unit cell of 25% yttrium-doped barium cerate (BCY25), comprised of oxygen (red), barium (green), cerium (beige), and yttrium (blue) ions. (b) P-band center vs. adsorption energy of oxygens within BCY25 configured along the vertical (○) and horizontal (□) axes. Horizontal oxygens with dashed outlines are coordinated to one yttrium. Vertical oxygens with dashed outlines are coordinated to two yttrium.
Additionally, this data supports a recent study by Yamazaki et al. that provides evidence for proton trapping within doped perovskites.\(^1\) The group found that proton-dopant association limits macroscopic proton transport within yttrium-doped barium zirconate. Protons bonded to yttrium-coordinated oxygen ions must overcome an additional association energy barrier of 29 kJ/mol (0.30 eV) to escape the dopant environment. This phenomenon can arise due to an electronic or geometric mismatch between the dopant and substituted ion.\(^1\) Our data provides evidence that protons are more stable on dopant-coordinated oxygen ions due to a shift in these oxygens’ p-band centers. This enhanced adsorption strength likely contributes to proton trapping that occurs within this and other perovskites. To determine the depth of proton trapping a simple analysis could be completed in a larger unit cell with a low dopant concentration. An analysis of the p-band centers of oxygens various distances from the dopant ions should provide valuable information about the depth the proton trapping effect has in the local environment. Overall, these results yield a valuable technique to identify dopant ions that may mitigate proton trapping effects. Researchers can screen for dopant ions that cause a minimal shift in the p-band centers of dopant-coordinated oxygen ions. Identifying perovskite-dopant systems that reduce proton preference for particular lattice sites should yield perovskites with enhanced macroscopic proton conductivities.

### 7.3.3 Proton Stability at the BaZrO\(_3\)-Metal Heterointerface

Building on the insights provided by the analysis of the BaZrO\(_3\)-vacuum interface, we now consider the more complex BaZrO\(_3\)-metal heterointerface. An example of a metal cluster at the BaO surface is depicted in Figure 7.8a, which also includes the three proton configurations probed in this study. The proton adsorption energies of these proton arrangements at the BaO-
vacuum and BaO-metal interfaces are displayed in Figure 7.8b, while the resulting proton stability changes due to the metal heterointerface are plotted in Figure 7.8c. The results show an overall improvement in proton stability due to the introduction of the metal at the BaO surface. The most pronounced enhancement in stability occurred in the first subsurface layer (Layer 2) for all the metals tested. Palladium showed the greatest increase in proton stability near the heterointerfaces, while stability owing to the remaining metals varied in different interfacial layers.
Figure 7.8 Analysis of proton stability at the BaO-metal heterointerface of BaZrO₃. (a) The unit cell of BaO-Pd heterointerface comprised of oxygen (red), barium (green), zirconium (light
blue), palladium (dark blue), and hydrogen (white) ions. (b) Adsorption energy plot of protons bonded to oxygen ions in the first three layers near the perovskite interfaces: BaO-vacuum (○), BaO-Ag (□), BaO-Ni (★), BaO-Pd (×), BaO-Pt (+). (c) The stability change between the BaO-vacuum and the BaO-metal interfaces. Symbols correspond to same metal heterointerfaces as given in (b).

Figure 7.9 depicts an example of a metal cluster at the ZrO₂ surface, as well as the hydration and stability results at the ZrO₂-metal heterointerfaces. Similar to the BaO-metal heterointerfaces, the greatest enhancement in proton stability occurs in the first subsurface layer of the perovskite slab, with the largest stabilizations occurring at the ZrO₂-Pd heterointerface. Here, Pt also shows a strong stabilizing effect. Ag and Ni also act to stabilize the proton, but their effects are about 50kJ/mol (0.5 eV) less than the Pt nanocluster.
Figure 7.9 Analysis of proton stability at the ZrO$_2$-metal heterointerface of BaZrO$_3$. (a) The unit cell of ZrO$_2$-Pd heterointerface comprised of oxygen (red), barium (green), zirconium (light blue), palladium (dark blue), and hydrogen (white) ions. (b) Adsorption energy plot of protons bonded to oxygen ions in the first three layers near the perovskite interfaces: ZrO$_2$-vacuum ($\bigcirc$), ZrO$_2$-Ag ($\square$), ZrO$_2$-Ni (*), ZrO$_2$-Pd ($\times$), ZrO$_2$-Pt (+). (c) The stability change...
between the ZrO$_2$-vacuum and the ZrO$_2$-metal interfaces. Symbols correspond to same metal heterointerfaces as given in (b).

To understand why the addition of metal to the perovskite interface leads to an enhancement in proton stability in the near surface environment, an electronic analysis of oxygen p-band center was completed. In this investigation, we were interested in comparing the adsorption energies and corresponding electronic trends between different BaZrO$_3$-metal systems. In previous electronic analyses, the p-band center was calculated with respect to the Fermi level of the system. Since the Fermi levels differ between each of the different BaZrO$_3$-metal systems, the Fermi level could not be used as a reference point. Thus, a reference atom (oxygen) was chosen on the bottom of the BaZrO$_3$ slab and was used to normalize each of the p-band centers for the different systems. Figure 7.10 depicts the p-band center analysis for the BaO-metal and ZrO-metal heterointerfaces.
Figure 7.10 Electronic analysis of proton stability at BaZrO$_3$ heterointerfaces. (a) Plot of p-band centers of oxygen atoms and their correlating proton adsorption strengths at BaO-metal heterointerfaces: BaO-Ag (□), BaO-Ni (★), BaO-Pd (×), BaO-Pt (+). (b) Plot of p-band centers vs. proton adsorption strengths at ZrO$_2$-metal heterointerfaces: ZrO$_2$-Ag (□), ZrO$_2$-Ni (★), ZrO$_2$-Pd (×), ZrO$_2$-Pt (+).

The data depicted in Figure 7.11 show a loose correlation between oxygen p-band center and proton adsorption strength when considering all of the systems tested. However, there is a clear deviation from this trend within the individual perovskite-metal systems. Upon a closer investigation into the geometrically optimized hydrated structures, it was found that the proton is uniquely stabilized by forming either an O-H--M bond (in Layer 1) or O-H--O bond (in Layer 2) near the metal heterointerface when compared to the perovskite-vacuum surface. The final configurations of protons in Layers 1 and 2 at the BaO-Pd surface are depicted in Figure 7.11. We hypothesize that the addition of the metal nanocluster on the uniform perovskite structure alters how neighboring ions stabilize the proton. For example, it is well documented for previous
computational studies that the perovskite lattice relaxes around a protonic defect, allowing the proton to form a weak hydrogen bond with a neighboring oxygen ions, forming an O-H--O bond.

![Figure 7.11 Optimized configurations of BaO-Pd heterointerfaces.](image)

The geometrically optimized configurations of protons in a) Layer 1 and b) Layer 2 at the BaO-Pd heterointerface (only first three perovskite layers shown). The proton in the first layer forms a O-H--Pd bond while the proton in the second layer forms a O-H--O bond to stabilize the proton within the lattice.

At the first layer of the metal heterointerface, the proton appears to form similar stabilizing bonds with the adjacent metal atoms. At the BaO-metal heterointerface, the proton in the first perovskite layer is oriented parallel to the interface (depicted in Figure 7.8). An analysis of the geometrically optimized structures reveals that in most cases the proton relaxes upward to form a weak bond with a neighboring metal atom. Figure 7.12 displays how the proton adsorption energy varied with resulting proton-metal bond length. The plot shows that the shortest bond distance occurred between the proton and Pd, a metal with a high affinity for hydrogen. This system corresponded to the strongest proton stabilization. The plots reveals a correlation between the O-H--M bond length and the proton adsorption energy on the first interfacial layer.
Figure 7.12 Effect of H-Metal bond length on proton adsorption energy. This plot displays how the adsorption energy of a proton configured in layer 1 of the perovskite-metal heterointerface varies with the length of the H-metal stabilizing bond. The BaO-metal systems tested included: BaO-Ag (□), BaO-Ni (⁎), BaO-Pd (×), BaO-Pt (+).

The p-band center model developed previously would not adequately predict this H-M stabilizing effect, as the model only relies on the electron distribution within the oxygen ions. Thus, it appears that the p-band center model cannot be used as a predictor for proton adsorption energy in systems that diverge from the uniform perovskite structure, such as the metal heterointerface. In other words, the existence of an additional stabilizing interaction with the proton at this interface is not accounted for by a p-band center metric that considers only a single proton-oxygen interaction. However, even in the near interfacial environments the p-band correlation still appears to be accurate. Figure 7.13 shows the same p-band center vs. adsorption energy data depicted in Figure 7.10, yet here the data is categorized differently. Instead of plotting the data by BaZrO$_3$-metal system, the data is plotted by the layer that the oxygen ion
resides in within the perovskite slab. For both the BaO and ZrO$_2$ interfaces, the p-band center model is inaccurate for the first interfacial layer, but the correlation between p-band center and adsorption energy can be seen in both layer 2 and layer 3 as the proton moves away from the complex interfacial environment.

(a)

(b)

Figure 7.13 Electronic analysis of proton stability plotted by perovskite slab layer. (a) Plot of p-band centers of oxygen atoms and their correlating proton adsorption strengths at BaO-
metal heterointerfaces for oxygens residing on Layer 1 (◇), Layer 2 (□) and Layer 3 (△) of the perovskite slab. (b) Same plot at the ZrO₂-metal heterointerface.

Despite the complexity of identifying the underlying cause of proton stability at the BaZrO₃-metal heterointerface, the results still present several potential implications to the broader perovskite field. First, the stabilization of the proton at the perovskite-metal heterointerface may contribute to the ability of protons to travel away from the TPB at the anode and toward the TPB of the cathode within fuel cell devices. Here we’ve identified that the metal interface that forms the TPB can act to stabilize protons at the surface compared to the perovskite-vacuum surface. Increased proton stability within the electrolyte may help drive the hydrogen oxidation reaction forward, as the protons can readily enter and diffuse into the electrolyte. Likewise, increasing stability at the cathode could decrease the barrier to proton diffusion out of the electrolyte, helping to drive forward the ORR. While the reaction mechanism must be favorable at the TPB for sufficient fuel cell performance to occur, it is also critical to identify metal catalysts that can also enhance proton mobility within the near TPB environments.

Additionally, these results may help explain an enhancement in proton conductivity observed upon the incorporation of Pd metal nanoparticles into the bulk of BZY. According to a study completed by Tong et. al, the Pd nanoparticles introduced into the perovskite during synthesis resided at the grain boundary of the perovskite oxide and caused an increase in both GB and overall conductivity. The group hypothesized that a band bending effect at the heterointerface increased proton concentration within the perovskite at the perovskite-metal junction. As it is widely accepted that proton concentration at the perovskite GB is low due to a positive GB core charge, the incorporation of the Pd nanoparticles into the GB may have increased the proton concentration within the region, thus increasing proton conduction. The
computational results presented above support this hypothesis by providing evidence that proton stability increases near the BaZrO$_3$-Pd heterointerface.

7.4 Conclusion

The goal of this work was to investigate proton chemistry at perovskite interfaces using \textit{ab initio} techniques. In the process, a critical relationship between oxygen p-band center and proton adsorption energy was identified. First, an electronic analysis at the BaZrO$_3$-vacuum surface revealed that oxygen ions with higher p-band centers yield stronger adsorption energies. This relationship between electron distribution and proton stability explains the fluctuations in adsorption energy in different layers of the BaO- and ZrO$_2$- near interfacial environments. Furthermore, this investigation revealed several important insights into proton chemistry at the perovskite surface. First, the instability of protons in the BaZrO$_3$’s first subsurface layers, as well as throughout the ZrO$_2$ near surface environment, reveals a potential barrier for proton mobility to the perovskite interface. This could lead to reduced proton conduction across perovskite GB interfaces previously attributed to a positive grain boundary core charge. Additionally, recent studies have used bulk parameters to describe and predict ORR catalytic activity on perovskite surfaces. This study reveals the electronic structure at the surface deviates from that of the bulk material. Thus, assessing surface properties may yield a better metric for screening for and designing perovskite catalysts with enhanced ORR catalytic activity.

Next, the relationship between p-band center and proton adsorption energy was examined in bulk yttrium-doped barium cerate to substantiate whether the p-band center model could be used to understand hydration trends between different perovskite systems. The results not only yielded the same correlations between the p-band center and proton adsorption strength, they
also led to an enhanced understanding of the implications of structural properties on material hydration. First, a study of 50%-doped BCY confirmed that divergence from the cubic perovskite crystalline structure produces two types of oxygen lattice sites. The disparate electron distributions between these sites leads to an enhanced proton stability on one type of site, likely leading to restricted proton mobility and decreased overall proton conductivities within these perovskites. Furthermore, an analysis of the 25%-doped BCY sample revealed that dopant-coordinated oxygen ions have higher p-band centers and, thus, increased proton adsorption energies. This finding provides evidence to support Yamazaki et. al.’s recent report of proton trapping in yttrium-doped barium zirconate by confirming preferential stabilization of protons around the dopant ions. The results from this study demonstrate how the p-band center can be used to understand variations in proton stability within disparate perovskite structures. Furthermore, it yields a simple parameter, which can be screened for \textit{in silico}, to identify and design perovskites with enhanced proton conducting capabilities.

Finally, an examination of various BaZrO$_3$-metal heterointerfaces revealed that the introduction of various types of metals at the perovskite surface may enhance proton stability near the perovskite interface. By using a reference atom to normalize the p-band density of states between the different metal systems, we found that the p-band center model developed previously in this study does not accurately predict adsorption energies of protons at the perovskite-metal interface. Upon examination of the geometrically optimized structures, it was determined that stabilization of the proton by the adjacent metal atoms influences the adsorption energy at the perovskite-metal junction. While the original p-band center model did not hold true for the protons in the top layer of the perovskite, its accuracy improved as the proton moved further away from the heterointerface. This finding suggests that alternative descriptors should
be sought to predict the influence of complex interfaces on proton chemistry in perovskite oxides. Despite the complications in understanding the proton stability trends observed here, the evidence for proton stabilization at the perovskite-metal heterointerfaces supports Tong et. al.’s hypothesis that the incorporation of metal nanoparticles into the perovskite can change the concentration of protons in the near heterointerface environment. By exploiting this principle, nanoparticles can be incorporated into regions of low proton conductivities to boost proton concentration and enhance proton conduction within perovskites.

7.5 References


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CHAPTER VIII

CONCLUSIONS AND FUTURE DIRECTIONS

8.0 Overview

This dissertation work has yielded new insights into proton and defect stability within perovskite materials as well as novel strategies to investigate proton chemistry within perovskite-type oxides. Density functional theory (DFT) was used throughout to gain an atomistic level understanding of proton stability in several different environments within polycrystalline perovskites. Using barium cerate (BaCeO$_3$) as a probe material, hydration thermodynamics were first explored in the uniform crystalline bulk to verify and examine hydration trends seen experimentally within the perovskite. Defect segregation was then investigated in the more complex interfacial environment to probe the origin of low proton conductivity across grain boundaries (GB). A comparison between BaCeO$_3$ and another common perovskite, barium zirconate (BaZrO$_3$), yielded a new strategy for how to mitigate the development of a positive GB core charge within perovskite oxides. Finally, a detailed examination of proton chemistry near the perovskite interface produced a higher level understanding for how electronic properties
influence hydration within perovskites. This study also identified how the introduction of a metal heterointerface can enhance material hydration in the heterointerfacial environment.

8.1 Bulk Hydration Investigation of Yttrium-Doped Barium Cerate

Perovskite oxides are a complex category of materials that enable chemical and structural tuning to manipulate various physical properties. For example, adding a dopant into the lattice can enhance hydration but may simultaneously decrease proton mobility within the material, influencing the two factors that contribute toward proton conductivity.\textsuperscript{1,2} There are numerous dopants that have the potential to alter perovskite properties, but it is too expensive and time consuming to experimentally synthesize all of the combinations of possible perovskite material and dopant types and concentrations. This motivates computational investigations of basic properties of perovskites to develop new methods to understand, predict, and screen for new perovskites with favorable hydration properties.

In Chapter 4, yttrium-doped barium cerate (BCY) was used as a probe material to investigate hydration properties within doped perovskites. Barium cerate (BaCeO\textsubscript{3}) exhibits amongst the highest proton conductivities within the class of perovskite oxide materials and thus is commonly used for detailed perovskite investigations. The aim of this study was to develop a hydration model of BCY from solely \textit{ab initio} strategies to not only understand the thermodynamic contributions to material hydration, but also to develop a strategy others could use to screen for how material variations affect hydration favorability.

First, DFT was employed to calculate the hydration enthalpy of BCY at three different dopant concentrations: 50\%, 25\%, and 12.5\%. The computed hydration enthalpy values for each doping level agreed well with experimentally-derived results, indicating that hydration enthalpy
decreases, or becomes more favorable, with increased yttrium doping. To understand this thermodynamic trend a Bader charge analysis was completed to examine how the introduction of yttrium ions alters the charge on the oxygen ions within the lattice. Our hypothesis, based on prevailing theories within the field,\textsuperscript{3} was that the substitution of the less electronegative yttrium species (compared to the replaced cerium atom) would lead to more negatively-charged oxygen ions. The resulting charge analysis supported this hypothesis, revealing that the average charge of oxygen ions in the higher doped materials retained a more negative charge, increasing the basicity of the oxygens and leading to more favorable proton bonding and material hydration.

Next, a statistical thermodynamic model was developed to predict hydration entropy as a function of dopant concentration. The basic entropy model included only configurational entropy, as this contribution to overall hydration entropy within perovskites was previously unknown. The resulting model captured the overall hydration entropy trend, indicating the entropy changes due to hydration become more negative, or more unfavorable, with increased yttrium doping. However, there was a large discrepancy between the calculated model and experimentally-derived values. Major assumptions within this model likely account for these discrepancies. For example, the model assumes that the protons within the lattice have an equal probability to reside on any oxygen ion. However, data suggests that protons may be more or less likely to reside on oxygen atoms surrounding dopant ions based on the size and electronic properties of the dopant ions.\textsuperscript{1,4} The model also assumes that dopant ions are evenly dispersed throughout the material, while recent studies support a segregation of dopant ions to various regions within the perovskite.\textsuperscript{5} Incorporating more complex factors, such as the increased activation energy for protons on dopant-coordinated oxygen, that influence proton configuration
within perovskite lattices may adjust for the discrepancy between this simple model and experimental results.

The computationally-derived enthalpy data and the statistical thermodynamic model of entropy were combined to provide an equation to calculate the extent of material hydration as a function of dopant concentration, temperature, and partial pressure of water. The final hydration model displayed similar trends as those seen experimentally, along with an additional result that suggests that maximum hydration within BCY will occur at a dopant concentration of 25%. There is no experimental data to validate this result because it is difficult to synthesize perovskites with dopant concentrations higher than 25%.1

While improvements should be made to this ab initio model of perovskite hydration, particularly in the hydration entropy model, this study still provides useful insights into the thermodynamics of material hydration. The results of this study verified experimentally-determined thermodynamic properties of material hydration, yielded an understanding of how configurational entropy contributes to overall material entropy, and contributed a method to computationally probe material properties in a relatively simple and cheap way.

8.2 Defect Segregation at the Perovskite Interface

Once proton stability was explored in the simple bulk crystalline region, we then went on to explore the more complex interfacial environments within the polycrystalline perovskite materials. Although BaCeO3 demonstrates amongst the highest proton conductivities of perovskite materials, BaZrO3 exhibits bulk conductivity that exceed even that of BaCeO3.1,6 However, the grain boundary conductivity of BaZrO3 is orders of magnitude lower than its bulk conductivity, resulting in slow proton conduction within the material.7-9 Recent work suggests
that the development of a positive grain boundary (GB) core charge contributes to this sluggish grain boundary conductivity.\textsuperscript{6-8} The positive core charge repels protons away from the grain boundary interface, decreasing proton concentration and conduction across this region. While researchers hypothesize that positive defects (such as oxygen vacancies) accumulate at the GB to form this charged interface, no evidence exists to explain the origin of the positive GB core charge.

The goal of this study was to compare the defect stability of positively charged oxygen vacancies and relatively negatively charged yttrium dopants at the BaCeO\textsubscript{3} and BaZrO\textsubscript{3} surfaces to better understand the development of a GB core charge within perovskite materials. While perovskite-vacuum surfaces do not accurately describe the GB region, they can provide an ideal environment in which to isolate stability trends of different defect species at the perovskite interface. By deleting the complex electrostatic interactions that occur in the GB environment, we can determine the fundamental factors that dictate interfacial defect segregation.

To begin, the most stable interfaces were chosen to complete the defect segregation study. However, while the structural stability of various BaZrO\textsubscript{3} surfaces had been established previously, there existed no such analysis of the BaCeO\textsubscript{3} interfacial structure. In Chapter 5, a surface stability study of orthorhombic BaCeO\textsubscript{3} was completed. The results suggest that the (001) BaO- and CeO\textsubscript{2}- surfaces are the most structurally stable. Shishkin and Ziegler suggest that the (001) surfaces are the most energetically favorable because they require the fewest number of bonds to be broken for the formation of the interface.\textsuperscript{10} A further analysis revealed that the non-stoichiometric (110) and (111) interfaces approached the stability of the (001) surfaces, owing to a large amount of surface reconstruction that was allowed due to ion vacancies at the crystalline surface.
Once the (001) surfaces were established as the most energetically favorable for both the BaCeO$_3$ and BaZrO$_3$ perovskites, the two defects (oxygen vacancies and yttrium dopants) were configured independently and then synergistically in the near interfacial environment. The results, described in Chapter 6, revealed that oxygen stability was strongly dependent on dopant segregation due to the favorable pairing between the defects. For example, dopants that segregate to the perovskite interface appear to increase the stability of oxygen vacancies in this interfacial environment, leading a positively charged surface. A further analysis of the system revealed that dopant-oxygen bond strength may influence the favorability of dopant segregation to the material surface. The results of this study suggest that synthesizing perovskites with strong dopant-oxygen bond strengths compared to the original metal-oxygen bond may lead to a decrease in dopant segregation to the interfacial regions. Less dopants at the perovskite interface may then decrease the stability of oxygen vacancies at the GB and weaken the positively charged GB core charge.

The results from this study have potentially significant implications in how researchers understand the origin of the positive GB core charge within perovskite oxides. Additionally, the findings suggest a simple screening technique with which to design perovskites to mitigate the development of this interfacial charge. First, a recent computational investigation of oxygen vacancy stability at the BaZrO$_3$ grain boundary suggested that oxygen vacancies are stabilized by electrostatic forces across the complex GB interface. However, the results of this study at the simple perovskite-vacuum interfaces demonstrated a similar stability trend, indicating that defect segregation at the GB interface may be more heavily determined by fundamental energetic driving forces near the perovskite interface. Furthermore, this study demonstrates that dopant ions may play a large role in stabilizing positively-charge oxygen vacancies at the perovskite
surface. This result suggests that decreasing the energetic favorability of dopants at perovskite interfaces may mitigate the segregation of oxygen vacancies to the GB region, decreasing the strength of a positively charged GB core. A simple bond strength analysis can screen for dopants with strong dopant-oxygen bonds that will reduce dopant segregation to the perovskite interface.

Future work should aim to identify the contributions that impact defect segregation at the more complex GB interface. While this study revealed that an implicit driving force for defect segregation might exist at perovskite interfaces, it would be advantageous to identify further contributions from the electrostatic interactions of the GB. A comparison between defect stability at various GB interfaces and simple perovskite surfaces may reveal structural or electronic effects that lead to additional defect segregation. This can be done by forming both a perovskite-vacuum and grain boundary interface with the same interfacial termination and comparing defect segregation trends between the two systems. Future work should also test the validity of the bond strength screening model. Researchers should use simple computational analysis to identify dopants with low dopant-oxygen bond strengths and test for enhancements in the GB conductivities of the experimentally synthesized perovskites. Furthering our understanding of the origin of the positive GB core and developing methods to screen for perovskites that mitigate this interfacial charge will help broaden the temperature range in which perovskites can be useful in electrochemical devices.

8.3 Proton Stability at Perovskite Interfaces

Finally, an investigation of proton chemistry at the perovskite interface aimed to provide a greater understanding of how proton stability changes at various interfacial environments. While research has identified important factors, such as dopant environment and lattice structure,
that influences hydration and proton mobility within the bulk, only recent work has been able to focus on the complex perovskite interfaces. Growing evidence that proton chemistry both near and at the interface influences both proton conduction and catalyst activity has motivated more thorough examinations of proton chemistry in these interfacial environments.\textsuperscript{7,13}

An analysis of proton stability at the (001) surfaces of BaZrO$_3$ revealed that protons stabilization fluctuates near the perovskite surface. While material hydration is not as favorable near the perovskite-vacuum surface as within the material bulk, there is a stabilization that occurs at the top surface layer. Proton adsorption in the first subsurface layer is about 0.5-1 eV less favorable than at the surface, providing a potential activation barrier for protons introduced at the surface to move into the material bulk. Fluctuations in stability become smaller as protons travel into the bulk from the surface.

An electronic analysis examined the density of states of electrons in the p-band of oxygens in different layers near the perovskite surface to probe why proton stability varied in the near interfacial environment. The results revealed a strong correlation between the proton adsorption energy of a given oxygen and its p-band center. As the p-band shifted higher toward the Fermi level, indicating more electrons available for bonding, the hydration enthalpy became more favorable. This analysis provides clear evidence for how electronic changes within the perovskite lattice influences the favorability of specific oxygen and overall material hydration.

An electronic analysis of oxygen ions within bulk yttrium-doped barium cerate revealed that the p-band center is a viable descriptor for proton adsorption strength in a variety of different perovskite environments. For each of the three tested dopant concentrations, 50\%, 25\%, and 12.5\%, oxygens with higher p-band centers yielded stronger hydration enthalpies. A closer examination of the 50\%-doped sample provided electronic evidence to explain low proton
conductivities in non-cubic perovskite lattices. The DOS results revealed that the orthorhombic lattice can be resolved into two different oxygen lattice sites. These two sites yield disparate p-band centers, thus creating more stable proton bonds with one type of oxygen than another and causing biased diffusion within the lattice. An additional investigation into the 25% doped BCY sample provided electronic evidence of proton trapping around the dopant ions within the lattice. Dopant coordinated oxygens yielded higher p-band centers and stronger proton adsorption energies.

Once the efficacy of the p-band center as a predictor for hydration enthalpy was verified, the analysis was used to assess the effects of a metal heterointerface on proton stability. The metal heterointerface is an important environment to study as perovskites often form a heterojunction within electrochemical devices at the triple phase boundary (TPB). The results indicated that palladium most effectively stabilizes protons near the heterointerface, particularly in the first subsurface layer where proton stability is weak at the perovskite-vacuum interface. An analysis of the p-band center revealed that this electronic descriptor does not accurately predict adsorption energy at the immediate perovskite-metal junction, as it does not account for the formation of stabilizing bonds that form between the proton and metal atoms. However, the model’s accuracy increases quickly as you move from the first perovskite layer into the second and third. The results from this study suggest that proton incorporation into the perovskite bulk may occur with a smaller activation barrier at the perovskite-electrode TPB as proton instability is diminished. Additionally, these results reveal that the incorporation of metal nanoparticles within the material bulk and grain boundary regions may increase proton concentration within the near heterointerfacial environment, potentially increasing proton conduction near these boundaries, as seen in a recent experimental study.14
There is much work that can be done to expand upon the compelling findings revealed in this comprehensive study. Future work should expand upon and test the bounds for the p-band center as a predictor of material hydration. Researchers can use this model to probe for dopants that reduce the origins of proton trapping, which is caused by increased proton bond strength in oxygens coordinated to dopant ions. By performing a simple DOS analysis on oxygens surrounding various dopants within a given perovskite lattice, perovskite oxides with reduced proton trapping can be identified and synthesized. Researchers can also use the p-band center to predict perovskite materials and surfaces that may yield favorable catalytic qualities by characterizing and tuning the adsorption strength on the material surface. Various perovskite surface and surface facets should also be probed to explore how proton stability changes on different surface configurations and in the near surface environments of various perovskite surface facets, such as the (110) and (111) terminations.

Finally, work should be done to identify either an alternative or a compounding parameter that describes proton adsorption energy at perovskite heterointerfaces, as our model was shown to be inaccurate in the BaZrO$_3$-metal study. This will involve a comprehensive analysis on proton bond formation with different metal atoms, which will also be influenced by the softness of the perovskite lattice. Furthermore, a more comprehensive study of the perovskite-metal interface should be completed using a variety of shapes and sizes of metal nanoparticles as well as a more comprehensive sampling of metals. Larger clusters should also be probed to examine whether proton stability near the boundary of the cluster (such as at the TPB) differs from the stability of the proton at a uniform perovskite-metal boundary (like that found at the interface of a metal nanoparticle within the perovskite lattice).
8.4 Summary

In summary, this *ab initio* investigation of hydration within model perovskite oxides has yielded a deeper understanding of proton and defect chemistry within various perovskite environments as well as useful screening techniques that can be utilized to identify perovskites with enhanced material properties. The methodology and experiments described in this thesis contribute to the field’s basic understanding of proton stability within the complex perovskite lattice, the origins of a GB core charge, and the correlation between electronic properties and material hydration. Future work expanding upon this thesis can use the novel screening techniques presented here to advance the field of perovskite oxides by identifying material dopants that may mitigate the development of a detrimental GB core charge and diminish the effects of proton trapping, creating perovskites with greater proton conduction capabilities.

8.5 References


CHAPTER IX

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CHAPTER I –


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CHAPTER II


**CHAPTER III –**


**CHAPTER IV –**


CHAPTER V –


CHAPTER VI –


**CHAPTER VII –**


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**CHAPTER VIII –**


