Novel Methods of Tritium Sequestration: High Temperature Gettering and Separation Membrane Materials Discovery for Nuclear Energy Systems

Reactor Concepts

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1. EXECUTIVE SUMMARY

1.1 Project Overview
This project is aimed at addressing critical issues related to tritium sequestration in next generation nuclear energy systems. A technical hurdle to the use of high temperature heat from the exhaust produced in the next generation nuclear processes in commercial applications such as nuclear hydrogen production is the trace level of tritium present in the exhaust gas streams. This presents a significant challenge since the removal of tritium from the high temperature gas stream must be accomplished at elevated temperatures in order to subsequently make use of this heat in downstream processing. One aspect of the current project is to extend the techniques and knowledge base for metal hydride materials being developed for the “hydrogen economy” based on low temperature absorption/desorption of hydrogen to develop materials with adequate thermal stability and an affinity for hydrogen at elevated temperatures. The second focus area of this project is to evaluate high temperature proton conducting materials as hydrogen isotope separation membranes. Both computational and experimental approaches will be applied to enhance the knowledge base of hydrogen interactions with metal and metal oxide materials. The common theme between both branches of research is the emphasis on both composition and microstructure influence on the performance of sequestration materials.

1.2 Project Objective
The research project uses theory based materials discovery in order to gain fundamental insights into hydrogen isotope effects in high temperature metal and metal oxide systems. This materials discovery effort will feed directly into the experimental portion of our proposed work. The initial nuclear energy application of this new knowledge will be in novel tritium sequestration using i) novel high temperature tritium gettering materials, and ii) high temperature proton conducting membrane separation materials.

1.3 Project Results and Key Findings
For the metal hydride study, density functional theory (DFT) calculations have been used to explore the predicted stabilities of ZrH2, HfH2, TiH2, LiH, and NaH metal hydrides with four levels of theory. We also investigate isotope effects to understand if these should be accounted for in screening of deuterated or tritiated materials. We show that calculations that account for vibrational corrections to the crystal lattice are not necessary to get an accurate description of relative stabilities of metal hydrides. The shifts in dissociation temperatures due to isotope substitutions are <50 K for all materials, with larger shifts for lighter materials, as expected. We show that accounting for vibrational effects due to isotope substitution in metal hydrides is unnecessary to accurately predict the relative stabilities of metal hydrides at high temperatures.

Zirconium based materials were chosen for hydrogen isotope sequestration study due to their high affinity for hydrogen and knowledge base regarding “activation” or surface preparation for hydrogen absorption. Zircaloy-4, a zirconium alloy was chosen for extensive testing in both 100% H2 as well as dilute 1% H2 balance He gas. The absorption of hydrogen and deuterium on a pure zirconium sample at elevated temperatures has been determined. we can conclude that at the temperature tested (600°C) that the maximum amount of hydrogen (or deuterium) that can be absorbed on the Zr sample is an H/M loading of 1.6 (moles of H atoms per moles of metal atoms). At 600°C the equilibrium pressure of H2 absorbed on Zr is roughly 1 torr for a loading of 1.6 and the partial pressure of H2 in the gas stream is 8 torr (1% H2 in He at 800 torr). The maximum loading of Zr is an H/M of 2.0 and the equilibrium pressure at this
loading at 600°C is 100 torr. Given that the equilibrium pressure is higher than the H₂ pressure in the gas stream the maximum loading of H₂ cannot be reached under our test conditions which simulate actual hydrogen removal from He gas streams in NGNP applications. The experimentally determined equilibrium pressure of H₂ and D₂ absorbed on Zr under dilute He/H₂ mixtures in this work can be used to in potential future work on engineered systems for hydrogen isotope capture in NGNP systems.

As to the high temperature proton conducting oxide materials aspect, we have developed several novel high temperature proton conducting metal oxide ceramics with better stability and improved proton conductivity. Novel complex perovskite structure Ba₂Ca₁.₁₈Nb₁.₈₂O₉₋δ based high temperature proton conducting ceramics have been proposed. The effects of Ce doping on the Ca and Nb ions in complex perovskite Ba₃Ca₁.₁₈Nb₁.₈₂O₉₋δ (BCN18) proton conductor have been evaluated. It has been found that cerium ions can be doped into both the Ca and Nb sites to form a single-phase complex perovskite structure when the sintering temperature is 1550 °C. Ce ions substituted with Nb ions enhances the electrical conductivity, especially the grain boundary conductivity. The highest conductivity has been obtained for a composition of Ba₃Ca₁.₁₈Nb₁.₆₂Ce₀.₂O₉₋δ (BC(NC0.2)), possessing a conductivity of 2.69×10⁻³ S·cm⁻¹ at 550 °C in wet H₂, a 78% enhancement compared with BCN18 (1.51×10⁻³ S cm⁻¹). The chemical stability tests show that Ce-doped BCN18 samples remain single phase after treated either in boiling water for 7 h or in pure CO₂ for 4 h at 700°C. This work has demonstrated a new direction in developing high temperature proton conducting materials that possess both high conductivity and good stability.

Microstructure modification of BaZr₀.₁Ce₀.₇Y₀.₁Yb₀.₁O₃₋δ and Ba₃Ca₁.₁₈Nb₁.₈₂O₉₋δ based proton conducting ceramics have been achieved and their influences on the proton conductivity have been evaluated. Microstructural modification of BaZr₀.₁Ce₀.₇Y₀.₁Yb₀.₁O₃₋δ prepared by co-precipitation method has also been studied via a novel two-step sintering method. Coprecipitation method has been adopted to prepare nano-sized BZCYYb precursors with an average particle size of 30 nm. By controlling the sintering profile, an average grain size of 184 nm was obtained for dense BZCYYb ceramics via the two-step sintering method, compared to 445 nm for the conventional sintered samples. The two-step sintered BZCYYb samples showed less impurity and an enhanced electrical conductivity compared with the conventional sintered ones.

First principles assessment of perovskite dopants for proton conductors with chemical stability and high proton conductivity has been explored. As an initial example, we performed DFT calculations for KTaO₃ (KTO). We studied the proton transfer and rotation mechanism in defect free KTO. We also studied the native point defects, and proton transfer mechanisms near oxygen vacancies with 2⁺ net charge. In this work we present first-principles calculations of proton migration in KTO using the VASP code. The transition path of the proton is determined by performing the nudged elastic band (NEB) calculations. Proton diffuses in KTO involving oxygen vacancies with 2⁺ net charge with a barrier of 0.15 eV. These oxygen vacancies function as an anti-trap in KTO.

We further used first-principles calculations to address this topic in doped BaZrO₃ with efficient methods to examine a wide range of possible dopants (Y, In, Ga, Sc, Nd, Al, Tl, Sm, Dy, La, Pm, Er, and Ho). These calculations correctly identify the doped BaZrO₃ materials that are already known to have favorable properties, but also identify a number of promising materials that have not been examined previously. We investigated the physical origins of the trends in chemical stability and proton mobility among the different dopants. Our data allows us to
consider several possible physical descriptors for characterizing doped perovskites as proton conductors.

Hydrogen permeation measurements have been done in Dual phase ceramic (SrCeYbO$_3$-$\delta$) and metallic (Pd, Rh) membranes in order to enhance the electronic conductivity and improve membrane separation efficiency. X-ray diffraction analysis indicated no secondary phases were formed concomitant with metal additions. Permeation testing has been initiated on SrCeYbO$_3$-$\delta$ and dual phase materials using a gas feed of 1% H$_2$ with balance He in order to simulate the hydrogen isotope contamination levels expected in NGNP He cooled gas streams.

Ni-BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ (BZCYYb) hydrogen permeation membrane has been fabricated and the hydrogen flux has been tested. Ni-BZCYYb powder was synthesized by sol-gel combustion method and Ni powder and BZCYYb powder were mixed and uniaxially pressed followed by sintering at 1440 °C for 10 h in 4% H$_2$/N$_2$ to obtain Ni-BZCYYb membrane. The membrane was tested in a customer-built set-up for hydrogen permeability measurements. Ni-BZCYYb membrane with and without CO$_2$ in the feed gas stream. In dry feed gas, when N$_2$ was replaced by CO$_2$, the hydrogen permeation fluxes increased by 2 times. In wet feed gas, the hydrogen permeation flux was also improved, but in less magnitude compared with that in dry hydrogen stream. Analysis of the exhaust feed gas showed considerable amount of CO and H$_2$O formation after CO$_2$ was introduced, accompanied by the decrease of H$_2$ concentration. The improvement of hydrogen permeation fluxes was ascribed to the increase of moisture content in feed gas, which acutely enhanced the proton conductivity of BZCYYb and hydrogen permeation flux of the membrane, especially in dry feed gas.
It is predicted that global oil production is likely to peak within the next 5 to 15 years. With declining global oil reserves and consequent concerns over the supply of liquid fuels, there is an increasing worldwide interest in the hydrogen (H\textsubscript{2}) economy and hydrogen technologies. In this scenario, hydrogen will be the main energy carrier, currency, and storage media. Gen IV systems such as the Very High Temperature Reactor (VHTR) can produce hydrogen from heat and water using thermochemical process, high temperature electrolysis, or steam reforming of natural gas thus acting as distributed hydrogen generation sites. The first-of-a-kind plant consisting of the combination of a VHTR and a hydrogen plant is known as the Next Generation Nuclear Plant (NGNP). A distinguishing characteristic of NGNP from established commercial nuclear plants is the presence of a thermal energy connection between the nuclear plant and a non-nuclear user of high-temperature heat. In NGNP, thermal energy is delivered from the core of the nuclear reactor to a downstream user without the intermediate conversion of thermal energy into electrical energy, and this is accomplished by heat transfer through heat exchangers and the bulk movement of heat transfer fluids (e.g., helium) through conduits. This heat can also be used in other thermodynamic power cycles or in industrial processes provided that the heat supplied by fluids used to cool the reactors is free from radiation contamination before passing from the nuclear plant to the commercial hydrogen/energy/industrial use station.

However, tritium is generated in the core of the reactor from the ternary fission of nuclear fuel and diffuses from the core materials into the primary helium coolant. Consequently, a crucial caveat associated with using the heat supplied by nuclear reactors is that it must be free from radiation contamination before passing from the nuclear plant station to the commercial hydrogen/energy/industrial use station. Tritium is relatively similar to hydrogen, so it can bind to OH as tritiated water (HTO) and make organic bonds (OBT) easily. HTO and OBT are easily ingested by drinking, through organic or water-containing foodstuffs. Although tritium is not a strong beta emitter and it is not dangerous externally, it is a radiation hazard when inhaled, ingested via food, water, or absorbed through the skin\textsuperscript{1}. Experiments have shown that trace levels of tritium and tritiated species are typically present at levels less than 1% in the sweep gas for solid breeder reactors. As a result, a major technical hurdle to the use of heat generated in Gen IV type reactors is the sequestration of tritium species from the helium gas stream.

One effective approach to capture tritium from the nuclear fission gas stream is through tritium getters, materials which can absorb tritium. Metal hydrides are widely used for tritium capture, processing and storage in nuclear energy industry\textsuperscript{2}. Typical metals used are uranium, titanium and zirconium. In addition, many hydrogen-absorbing compounds such as LaNi\textsubscript{5}, ZrNi and Zr(V\textsubscript{x}Fe\textsubscript{1-x})\textsubscript{2} have been developed as tritium getters for effective utilization of hydrogen energy resources\textsuperscript{3}. Unfortunately, existing tritium getters typically work at low temperatures, usually less than 500 °C. Therefore, the exhaust hot gas stream from the NGNP reactors (expected to be around 850 °C) needs to be cooled down to lower temperature appropriate for tritium gettering and consequently the heat available to be captured and utilized in hydrogen production will be substantially reduced. This situation creates a pressing need for new materials development and discovery in order to allow tritium sequestration in processes that do not waste the heat available in these exhaust gases.

2.2 Background

One potential strategy to overcome the limitation of in-situ tritium sequestration in Gen IV reactors is to develop gettering materials capable of operating at high temperatures. Using
theoretical screening techniques, new compositions of mixed metal hydrides can be potentially evaluated for high temperature thermodynamic stability. The proposed efforts to develop new materials for high temperature tritium gettering will take advantage of technical advances that have taken place in recent years in the search for metal hydrides for hydrogen storage applications. In the latter area, the community has aimed to develop materials that release \( \text{H}_2 \) from metal hydrides at low temperatures. An important part of this work will be to use quantum chemistry calculations to provide thermodynamic information about large numbers of metal hydrides for which this information is not readily available. First principles calculation will be applied to develop fundamental thermodynamic information about a large collection of metal hydrides with the aim of identifying materials that are stable hydrides under the challenging operational conditions required for high temperature gettering. An inevitable feature of using computational methods to screen materials for a complex application is that these models cannot make predictions about all material properties that may be relevant in an actual application. For example, it is not able to predict the formation of materials if their crystal structure is not known and included in the database for the first principles calculation. This implies that efforts to synthesize and determine the structure of new complex metal hydrides remain crucial to the search for high-performance materials. In addition, it is not feasible to consider in detail how a large number of materials will respond to impurities in the gas stream to be processed. Consequently, such material properties must be assessed experimentally. The key goal of the computational screening, therefore, is to provide reliable predictions about a large number of materials so that experimental efforts can be focused on materials with the greatest probability of success.

A second potential strategy to overcome the limitation of tritium sequestration in situ from the NGNP gas stream is application of a high temperature hydrogen-pump using dense membrane technologies. Following the discovery of proton conduction in perovskite ceramics such as \( \text{SrCeO}_3 \) by Iwahara in 1981, dense ceramic membranes have received much attention due to their low cost and high efficiency in hydrogen gas separation applications\(^4\). This approach has recently been employed in the fusion community in the International Thermonuclear Experimental Reactor (ITER) project for tritium removal from helium cooled gas streams in order to be recycled back to the fusion reactor\(^5\). In these initial studies, high temperature proton conductors are used as the electrolytes for electrochemical hydrogen pumps as shown in Figure 2.1. When an electrochemical cell of a proton conductor is constructed and a direct current is applied to the cell, hydrogen (and its isotopes) in the anode compartment can be electrochemically pumped to the cathode by the following electrode reactions:

\[
\begin{align*}
\text{H}_2 & \rightarrow 2\text{H}^+ + 2\text{e}^- \text{ (anode)} \quad (2.1) \\
2\text{H}^+ + 2\text{e}^- & \rightarrow \text{H}_2 \text{ (cathode)} \quad (2.2)
\end{align*}
\]

The hydrogen pumps described above employ proton-conducting electrolytes that have negligibly low electronic conductivity under operation, thus requiring an externally applied power source to drive the hydrogen separation. The performance characteristics of this process using \( \text{CaZrO}_3 \) based ceramics at 800°C using a permeation surface area of 47cm\(^2\) were reported to be effective for extracting dilute hydrogen from hydrogen/argon mixed gas streams. Gas streams with 0.1% hydrogen were completely separated with hydrogen removal rates of 0.2ml/min at 2.5V applied bias (20mA current)\(^6\). The driving force for hydrogen (tritium) motion is the external bias applied across the two electrodes on the ceramic membrane and tritium can be extracted from the hot exhaust gas stream. Enhanced protonic conductivity is preferred for the hydrogen pump using the ceramic membrane in order to minimize ohmic loss and improve
hydrogen permeation rates. In order to construct such a framework for understanding hydrogen isotopes in oxides, first-principles calculations will be initiated, aimed at understanding fundamental aspects of proton conduction in the model system strontium cerate \( \text{SrCeO}_3 \). Little is currently known about the mechanisms of proton transport in these materials, so elucidating the rate limiting processes for these materials will provide useful opportunities for rational engineering of materials compositions to enhance proton transport rates. Density Functional Theory (DFT) will be applied to examine proton binding and hopping in stoichiometric and doped perovskites. A continuum model of proton and electron conduction will be established to analyze the important role of charged defects in the net transport of protons through the high temperature protonic conducting ceramics. New proton conducting materials with different dopant elements will be experimentally synthesized and the proton conductivity measured.

![Figure 2.1 Principle of electrochemical hydrogen pump using proton conducting ceramic.](image)

2.3 Research Plans
2.3.1 First principles calculations on high temperature metal hydrides as gettering materials

Motivated by extensive studies of light metal hydrides, computational screening of gettering materials will proceed in two stages. In the first stage, the thermodynamics of a large number of materials will be estimated using DFT calculations that require only the total energy of the hydride and the relevant dehydrided material. This approach does not explicitly include the effects of vibrational entropy or zero point energies in the solid phases, but careful comparisons with well-known materials have shown that these calculations can predict finite temperature reaction enthalpies with an accuracy of \( \pm 15 \text{ kJ mol}^{-1} \text{ H}_2 \). Because the entropic contributions associated with \( \text{H}_2 \) release from a solid hydride are dominated by the gas phase \( \text{H}_2 \), having a reliable estimate of the reaction enthalpy is sufficient to predict the material’s reaction thermodynamics. For materials that are predicted to have potentially useful reaction enthalpies, a second stage of calculations will be performed. In this stage, DFT calculations will be used to determine the vibrational density of states (VDOS) of the relevant solid phases. Once this calculation is complete, an accurate estimate of the material’s reaction thermodynamics is possible. Computing the VDOS is much more computationally demanding than the simpler total energy calculations, so screening materials using this two stage process will make it possible to efficiently describe a large number of materials.

2.3.2 High temperature gettering materials synthesis and evaluation

Commonly used techniques for the manufacture of metallic gettering materials include induction melting and casting, followed by pulverization if necessary. The casting process for intermetallic materials synthesis is simple in principle, but is fraught with complexities. Ideal
casting conditions for single-phase ternary intermetallic alloys require high thermal gradients and extremely low growth rates (during solidification) to obtain a homogenous, segregation free alloy. These are difficult to achieve in practice, hence conventional casting technologies leads to alloys consisting of coarse dendrites which is non-homogenous and with some degree of segregation. Once the alloy is pulverized, this results in variation in the chemistries and microstructure within the particulate hydrides. This could lead to differences in efficiencies and reliability in final application.

This project will address the challenges in synthesis of high temperature metallic gettering materials by examining rapid solidification technologies (RST). RST is an advanced materials technology that has been developed in order to achieve novel processing induced micro/nanostructures and has been adapted recently to a broad range of alloys including intermetallics. RST involves melt spinning alloys into thin foils or atomizing into powder at rapid cooling rates. The material that results has extremely fine microcrystalline, nanocrystalline or even glassy metallic structure. Following this casting the materials may be processed to optimize their microstructure by either heat treating or mechanical processing (mechanical milling or plastic deformation).

Once new materials are identified and synthesized, performance testing with hydrogen and hydrogen isotopes will be conducted via existing flow through reactor testbeds developed for tritium benchmark studies at the National Lab Partner. Potential challenges for hydrogen isotope getters are their susceptibility to irreversible and exothermic reaction with common species such as oxygen and water. Hydrogen purification and capture experiments will be performed in both static (equilibrium of gas with metal hydride) and dynamic (flow through gettering) modes. An impurity generator will be used to introduce low levels of impurities into helium gas streams for process validation. In the static mode, a given amount of metal hydride will be exposed to a pressure of the gas composition of interest over a function of time monitoring the final pressure state of the system. After equilibrium is achieved the gas space will be evacuated followed by heating of the metal hydride with concurrent monitoring of the pressure rise due to desorbed hydrogen species. In the dynamic mode, the metal hydride getter material of interest will be placed in a packed bed flow-through reactor and the inlet/outlet gas stream concentration will be measured via mass spectroscopy as a function of flow rate, temperature, and the number of flow-through cycles.

2.3.3 Fabrication of potential high temperature proton conducting ceramics

The electrical properties of the high temperature perovskite type protonic conducting ceramics are greatly influenced by the crystal structure and microstructure of the material. In general, applications of the ionic conducting materials start with the synthesis of the corresponding ceramic powders, and the conventional solid state reaction route is often applied. In this method, different kinds of metal oxides and/or carbonates mixed in stoichiometric ratio to yield a given composition are ball-milled, ground and fired at high temperatures. Such a synthesis method often leads to the following disadvantages: (1) a micro-homogenous phase structure is very difficult to obtain due to large and strongly bonded powder agglomerates; (2) contamination can hardly be avoided during milling and grinding, resulting in detrimental effects on the electrical conductivity; and (3) the mechanically ground mixture requires prolonged calcination at high temperatures (usually >1400°C), which is undesirable in the fabrication of dense fine grained ceramics due to the promotion of abnormal crystallite growth. We will attempt to synthesize high temperature proton conducting powders using a sol-gel technique.
Compared with the conventional solid-state reaction method to synthesize high temperature protonic conductors, the advantage of a sol-gel technique with the help of chelating ligand is that the constituent metal ions are mixed at the atomic level in the solution so that nano-sized precipitates can be formed by controlling the precipitation parameters such as temperature, solution concentration, nucleation and growth kinetics of the precipitate as well as pH value of the solution. The sol-gel technique is an ideal method to produce nanosized proton conductor powders which can be used to make thin film ceramic membranes for hydrogen and hydrogen isotope permeation.

While substantial work has addressed and continues to address the interplay between electronic and ionic conductivity in oxygen ion conductors, less attention has been paid to proton conducting oxides. The National Lab Partner has extensive experience in handling and storing hydrogen gas in both the nuclear and commercial sectors and is interested in exploring proton conducting ceramics for applications in isotope sensors, hydrogen separation membranes and catalytic reactors. Our team’s unique capability to study the conductivity and transport properties of proton conducting materials under different hydrogen isotopes is expected to lead to significant improvements in the understanding of hydrogen incorporation and transport through ceramic oxides. This portion of the proposed effort therefore approaches the problem by focusing on i) hydrogen separation membranes and ii) surface exchange and transport measurements of hydrogen isotopes to address both the fundamental issues of heterogeneous material behavior. The hydrogen concentration gradients on each side of a proton conducting membrane are correlated with the hydrogen flux through the membrane by the Wagner equation:

\[
J_{H_2} = -\frac{RT}{16F^2L} \int_{\ln P_{H_2}^\prime}^{\ln P_{H_2}^\prime\prime} \frac{\sigma_e \sigma_n}{\sigma_e + \sigma_n} d \ln P_{H_2}
\]  

where \( J_{H_2} \) is the permeation flux of gas (mol/m² s), F is the Faraday constant, R is the gas constant, L is the thickness of the ceramic membrane, \( \sigma_e \) and \( \sigma_n \) are the electronic and ionic proton conductivities and \( P_{H_2}^\prime \) and \( P_{H_2}^\prime\prime \) are the gas partial pressure on the hydrogen rich and hydrogen lean sides of the membrane, respectively. Along with improvements in ambipolar electronic and proton conductivity over the partial pressure range, another possible enhancement for hydrogen flux is by reducing the membrane thickness. In contrast to the conventional high temperature protonic conductors that have significant literature established on processing and properties, mixed proton-electronic conductor materials demonstrating high hydrogen flux are not well known. The major concern relates to the availability of suitable proton conductors with high proton flux rates and which are stable at the operating temperatures (∼ 850 °C) and total pressures (∼ 25 bar). In addition to composite metal/ceramic materials, the microstructure of ceramic materials has been shown to impact the electronic conductivity and ultimately the gas separation properties of these materials. Other major challenges relate to ensuring that the materials used have adequate mechanical strength and toughness, that chemical and thermal compatibility exists between metal and ceramic phases, and that the fabrication and optimization of the microstructure can provide dense, defect-free thin membranes. A major outcome of this project will be a framework for fundamental understanding of proton transport in oxides at elevated temperature and partial pressure gradients relevant to hydrogen isotope separation. This framework will allow both the theoretical and experimental examination of the question “is a metal phase in conjunction with an oxide ceramic truly needed?”, or are there exist novel oxide structures with the concomitant ionic/electronic properties required for proton transport in hydrogen isotope separation conditions.
2.3.4 First principle calculations in search of desirable high temperature proton conducting ceramics

An important feature of the tritium process outlined above is that proton-conducting ceramics in this process will exist in equilibrium with very low partial pressures of oxygen. This observation suggests that defects related to O atoms in these ceramics will be prevalent, and it is likely that these defects will play a central role in the net rate of proton transport. To quantitatively characterize these effects, we will use energies calculated from DFT in combination with ab initio thermodynamics to predict the equilibrium concentration of defects in high temperature proton conducting ceramics at temperature and pressure relevant for tritium processing. Our calculations will examine a variety of defects (vacancies, divacancies, etc.) in several possible charge states.

Once the relevant defects in proton conducting ceramics have been established, DFT calculations will be used to examine the mechanisms associated with proton hopping through these materials. It will be important to determine whether localized defects in the perovskite form strong trapping sites for protons. If trapping of this kind does take place, then the long range transport of protons is likely to be dominated by the energy required by a proton to escape from a defect site. For each microscopic process examined in our calculations, the nudged elastic band method will be used to rigorously locate the transition states for hopping of protons between nearby energy minima. Once the energy minima and transition state and the vibrational frequencies associated with these states are known, efficient methods exist to estimate the contribution of tunneling to net hopping rates. Although it seems likely that the importance of tunneling for tritium transport at elevated temperatures is negligible, our calculations will allow us to directly examine this hypothesis.

We will also perform similar calculations to examine the properties of the dopants. In these materials, dopants can influence proton transport in multiple ways, including net expansion/contraction of the crystal lattice, potentially trapping of H near dopant sites, and changes in the population of O-related defects. Until detailed calculations are performed, it is challenging to know which of these effects will play a dominant role in a material’s performance. We aim through our calculations for these specific materials to provide a theoretical framework that will make it possible in the future to rationally consider other possible dopants to enhance proton conduction in perovskite materials.

In composite membranes made from ceramics and metal alloys, more than one avenue exists to allow net tritium transport across the membrane. Tritium can of course hop through the proton-conducting ceramic portion of the membrane, aided by electron conduction through the metal portions of the membrane. If Pd-based alloys are used for the metal portion of these composite membranes, however, tritium could also be transported through the membrane as an interstitial species in the metal. This kind of interstitial transport is the physical phenomenon that allows dense metal films to be used as hydrogen purification membranes. Considerable experience in using first-principles approaches to describe the net flux of H and its isotopes through Pd-based alloys has been gained in the University Partner One. We will extend this previous work in two directions that will provide guidance in our development of composite membranes. First, we will develop mesoscale models of composite membranes that account for proton/interstitial transport in both ceramic and metallic phases. In these models, the chemical potential of tritium will be assumed to be continuous at each ceramic/metal interface and tritium diffusion rates within each phase will be described using results from first-principles calculations. These models will allow us to explore the influence of phase morphology in these
composite membranes and to understand how the two phases in the membrane contribute to net tritium transport. Second, we will use DFT calculations to understand whether the presence of the metallic phase leads to doping of the ceramic phase with atoms from the metal at a significant level. If the equilibrium concentration of Pd atoms (in the case of a pure Pd metal phase) is calculated to be significant relative to the other defects that will have been quantified in the calculations already described above, then we will explore the role of these metal-induced defects on tritium mobility in the ceramic phase.

2.3.5 Proton transport property and hydrogen and isotopes permeation characterization

Utilization of high temperature proton conducting materials in devices requires careful mapping of the conditions and the defect chemistry required for pure protonic conducting as well as mixed proton and electronic conducting membranes for hydrogen separation. In the SrCeO$_3$-based system, oxygen vacancies are formed as a result of the charge balance due to the substitution of lower valent cations (e.g. Yb$^{3+}$) into the Ce$^{4+}$ lattice positions, resulting in oxygen vacancy formation in order to maintain charge neutrality. Proton conduction is enabled by formation of hydroxyl groups under humid atmospheres as a result of the oxygen vacancies. At high temperatures, desorption of water takes place, often accompanied by migration of oxygen vacancies in the crystal lattice. In oxidizing atmospheres, the oxygen vacancies may be compensated by formation of holes while reduction of oxygen and cerium ions may also take place at low oxygen partial pressures. Consequently, the conductivity and defect properties are highly dependent on atmosphere and temperature. Thermogravimetric analysis (TGA) will be applied to monitor the oxygen nonstoichiometry of the sample and x-ray photoelectron spectroscopy (XPS) will be used to study the valence states of the cerium ions at different environment on the SrCe$_{1-x}$Yb$_x$O$_3$ samples. These results will be directly compared to our DFT-based calculations for the same materials.

![Figure 2.2](image)

**Figure 2.2** Schematic illustration of set-up used to measure hydrogen flux through cermet membranes.

Once materials with high proton conductivity and chemical stability have been identified, they will be made into samples for hydrogen and isotopes permeation evaluation. These tests will be accomplished in a ceramic membrane reactor enclosed in a vertical tube furnace with gas chromatograph and mass spectroscopic (GC/MS) techniques used to quantify hydrogen concentration on both sides of the membrane, as shown in Figure 2.2. In addition, the
membranes’ stability in high temperature and tritium environment will also be tested. GC/MS techniques for thin film permeation measurements have been successfully demonstrated by the National Lab Partner in both metallic and metal oxide systems.

2.4 Results and Key Findings
2.4.1 DFT screening methods that accelerate materials development for hydrogen in metals applications

Figure 2.3 Illustration of computational methods to predict thermodynamically interesting metal hydride destabilization reactions for the Li-Al-H system for $P_{H_2}=1$ bar $H_2$.

Figure 2.3 shows this process schematically. In the Li-Al-H system, a library of known compounds is generated that can form from the elements, and crystal structures are relaxed using DFT to obtain $U_0$. The $U_0$ library is fed to the GCLP algorithm, which loops over the desired $\mu_{H_2}$ range and elemental ratios in small incremental steps to predict stable states. If changes to this stable mixture are tracked with temperature, equilibrium reactions can be written as shown for Li$_3$AlH$_6$.

Figure 2.4 describes a key result from the large scale computational screening by Kim et al. that identified 74 promising single-step reactions that met initial gravimetric (>6 wt % $H_2$) and enthalpic targets ($15 \leq \Delta H \leq 75$ kJ mol$^{-1}$ $H_2$). Crucially, 57 of the reactions were not previously predicted in the earlier work by Alapati et al. because they involved intermediates such as B$_{12}$H$_{12}$ species not then known to exist. The accuracy of these predictions depends heavily on the completeness of available materials databases with solved crystal structures.
Noted in Fig. 2.4 are reactions that proceed via a \( \text{B}_{12}\text{H}_{12} \) intermediate, involve refractory materials, or contain carbon, which may have kinetic limitations or form \( \text{CH}_4 \) at low temperatures. Three interesting single-step reactions are highlighted including a previously analyzed 2:1 mixture of \( \text{MgH}_2: \text{Mg(NH}_2 \) with \( \sim 7.4 \) wt% \( \text{H}_2 \) and \( T_{\text{est}} = 160 \) K and an unexplored 2:1:1 mixture of \( \text{LiNH}_2: \text{LiH}: \text{KBH}_4 \) with \( \sim 7.4 \) wt% \( \text{H}_2 \) and \( T_{\text{est}} = 300 \) K. The direct decomposition reaction of \( \text{MgH}_2 \) is also identified, but it is known that this material has slow kinetics and high \( T_{\text{est}} \). Further filtering and tightening of constraints to parse the large number of possible reactions enabled Kim et al. to additionally identify 23 promising multi-step reactions.

There are several caveats and limitations associated with the applied Grand Potential approach to screening for interesting metal hydride reactions in addition to those usually mentioned in conjunction with DFT or numerical calculations (i.e., the exchange-correlation functional, convergence, etc.). A key limitation highlighted earlier is that the methods cannot make predictions about reactions that include compounds missing from the materials library. As new compounds are identified, the calculations will need to be updated, but this should be straightforward as the algorithms for doing so are well-developed. Additionally, we are typically limited to studying compounds with complete crystal structures and atomic positions resolved, no partial site occupancies, and unit cells less than about 400 atoms. Current DFT methods that examine these excluded materials individually or that predict new materials are, at present, too costly for rapid screening applications.

A key assumption of the GCLP method is that it finds mixtures of compounds that minimize the overall system free energy, i.e., the compounds that lie on a so-called convex hull. Interesting element systems can be studied at higher levels of theory, but the errors for low to moderate temperature systems are still about \( \pm 10 \) kJ mol\(^{-1}\) \( \text{H}_2 \) compared with experiments. Uncertainty in the calculations arises primarily from the inexactness of the exchange-correlation functional and is unavoidable with DFT-based methods.

The GCLP as originally developed cannot detect metastable reaction paths that have free energies similar to those of the ground state system. Kim et al. developed a method for incorporating uncertainties inherent in DFT data to identify thermodynamically plausible alternate reaction pathways. To give one example, the 2:1:1 mixture of \( \text{LiNH}_2: \text{LiH}: \text{KBH}_4 \) identified in Fig. 2.4 has a GCLP-predicted reaction path

\[
\text{LiH} + 2\text{LiNH}_2 + \text{KBH}_4 \leftrightarrow \text{Li}_5\text{BN}_2 + \text{KH} + 4\text{H}_2 \\
(7.48 \text{ wt}\% \text{H}_2)
\]  

Figure 2.4 shows van’t Hoff plots and reaction free energies relative to the lowest energy path, \( \Delta\Delta G \), for eight possible metastable reaction paths (labeled 1-8) for these reactants. An analysis that accounted for zero point and vibrational free energy corrections to the DFT ground state energies indicated that for high temperatures or pressures, the reactants decompose via Eq. (2.5) (labeled as 1 in Figure 2.4(b)), but for low temperatures or pressures the predicted reaction pathway is

\[
\text{LiH} + 2\text{LiNH}_2 + \text{KBH}_4 \leftrightarrow 2\text{LiH} + \text{LiNH}_2 + \text{BN} + \text{KH} + 2\text{H}_2 \\
(3.74 \text{ wt}\% \text{H}_2)
\]  

(labeled as 2 in Figure 2.4(b)), which has a much lower hydrogen capacity. For these two reactions, \( \Delta\Delta G \leq \pm 10 \) kJ mol\(^{-1}\) \( \text{H}_2 \), across the \( T, P \) spectrum. Kim et al. concluded that DFT does not give absolute predictions of thermodynamically-preferred decomposition reactions for this system since the competing paths are too close in energy. Including this kind of assessment of uncertainty in DFT-based predictions is valuable, especially in systems like metal hydrides where kinetic limitations may influence experimental observations.
Figure 2.4 (a) van’t Hoff plot for the eight (labeled) possible decomposition reactions predicted using metastability analysis in 2 LiNH$_2$ : 1 LiH : 1 KBH$_4$ mixture (b) Reaction free energies relative to low energy path.

Figure 2.5 illustrates key steps for computing the permeability of hydrogen through a candidate dense metal membrane using DFT calculations. DFT calculations typically recover qualitative permeability trends with respect to composition and temperature and can be expected to perform well for screening purposes when membrane transport resistances are dominated by bulk properties. The primary challenge for describing hydrogen solubilities and diffusivities in crystalline alloys is the frequent substitutional disorder of the metal atoms. This leads to a large library of local interstitial environments that H can encounter for which binding energies must be computed. Cluster expansion (CE) methods have been developed to help resolve this. Providing reasonable quantitative accuracy, these methods use large libraries of interstitial site binding and transition-state energies to develop a lattice model. Once the lattice model is determined, hydrogen solubility and site hop rates are computed. These rates are then fed to a
kinetic Monte Carlo calculation to predict the self-diffusivity of hydrogen through the metal lattice. The identification of transition states is the most computationally intensive bottleneck in Figure 2.6 when computed using methods such as the Nudged Elastic Band approach. However, the computational cost can be greatly reduced if transition states can be located based on geometric or symmetry considerations.\textsuperscript{13} Only an initial alloy crystal structure is required to predict the permeability of hydrogen in metal alloys with these methods.

\textbf{Figure 2.5} Illustration of detailed first principles model to compute hydrogen permeability through crystalline metal membranes

Figure 2.6 shows several alloys that are predicted to have normalized permeabilities greater than one, i.e., larger than that of pure Pd at 600 K. For example, DFT predicts that Pd\textsubscript{96}Y\textsubscript{4} films have permeabilities for hydrogen \textasciitilde{}2.3 times larger than pure Pd at 600 K. Experimentally, similar compositions have produced films with \textasciitilde{}4.5 times enhanced performance for 573-623 K.\textsuperscript{14} Interestingly, the screening calculations identify Pd\textsubscript{96}Tm\textsubscript{4} (a previously untested material) as a significant improvement over pure Pd for hydrogen permeance. Fabrication and testing of a Pd\textsubscript{95.5}Tm\textsubscript{4.5} film between 673 K and 773 K showed that the Pd-Tm film had higher permeability than either pure Pd or the industry standard Pd\textsubscript{80}Ag\textsubscript{20}. Though absolute agreement with experimental permeabilities is not guaranteed, this work illustrates that DFT-based characterization of dense metal membrane hydrogen transport can be accessible from a computational intensity perspective and, critically, can identify new materials with enhanced properties.
Figure 2.6 DFT-predicted permeability of Pd$_{96}$M$_4$ fcc alloys at 600 K normalized by the permeability of pure Pd as a function of simulated lattice constant. The solid black line indicates the permeability of pure Pd.

Figure 2.7 DFT-predicted solubilities (H/M hydrogen/metal atom) at 600 K for 57 intermetallics. The volume/metal atom for pure Pd is 15.9 Å$^3$. The inset shows an expanded view of the solubility for volumes between 12 and 18 Å$^3$. The black solid line and the red dashed line in the inset show the favorable solubility range used to screen candidates ($10^{-1}$-$10^{-5}$ H/M).
DFT-based methodologies have also been used to screen Pd-based intermetallics with discrete, ordered compositions. Intermetallics have potential to exhibit improved resistance to contaminants due to the enhanced thermodynamic stabilities of these materials relative to the disordered solid solutions discussed previously. Chandrasekhar et al. predicted hydrogen permeabilities for 78 binary Pd-based intermetallics and also identified those intermetallics with the tendency to form hydrides with implications for hydrogen embrittlement. Figure 2.7 displays the computed solubilities for 57 intermetallics. Solubility was used as a first screening parameter to identify interesting materials at the target temperature. The solubility of pure Pd is shown as a reference.

The models developed to predict H permeabilities through these intermetallics are similar to those used for pure Pd, for which the predictions are in reasonable quantitative agreement with experiments. Based on this, Chandrasekhar et al. conclude that the predictions made for the intermetallics are sufficiently accurate to eliminate unfavorable materials, despite lack of experimental corroboration. The screening criteria account for DFT-induced uncertainties in calculated values, making the predictions useful for identification of materials with enhanced H permeabilities.

**Figure 2.8** Gaussian model parameters for H binding energy from detailed DFT calculations (blue, red, and green symbols) and the optimized parameters from fitted results for Zr\textsubscript{x}Cu\textsubscript{y}Ti\textsubscript{100-x-y} (black circles). Element labels indicate the T element in samples of Zr\textsubscript{30}Cu\textsubscript{60}Ti\textsubscript{10}.

Recent efforts have extended the computational methods for crystalline metal membranes to amorphous materials. Amorphous membranes lack the long range ordering of crystalline materials and have several advantages such as increased resistance to hydrogen embrittlement or sintering and potential lower costs relative to Pd-based materials. Several systems have demonstrated H\textsubscript{2} permeabilities on par with pure Pd.

Transport of H through amorphous materials is challenging to model because the identification of interstitial sites and transition states is no longer straightforward. A crucial deviation from crystalline behavior is that the solubility of hydrogen in amorphous materials can no longer be considered dilute due to very stable binding sites. Thus, we must correct the diffusivity for hydrogen concentration dependence, taking into account repulsive H-H interactions. Detailed methods that address these issues with DFT for amorphous membranes...
have been described and validated experimentally for amorphous Zr$_{36}$Ni$_{64}$ and Zr$_{30}$(Ni$_{0.6}$Nb$_{0.4}$)$_{70}$.\textsuperscript{18}

The original methods of Hao and Sholl are computationally expensive and not easily adapted for large scale screening. As with the calculations for crystalline materials, much computational effort is expended in locating the transition states and computing binding energies. Hao and Sholl describe a phenomenological model in which a Gaussian distribution is used for interstitial binding energies and a correlated saddle point model accounts for interstitial hop transition state energies. This approach means that only the distribution of interstitial binding energies has to be determined with DFT to qualitatively predict a membrane’s performance, a large reduction in computational effort.

Illustrating this approach, Hao and Sholl performed detailed calculations for amorphous Zr$_{30}$Cu$_{60}$Ti$_{10}$ (T=13 elements) and for Zr$_x$Cu$_y$Ti$_{100-x-y}$ as a function of composition. Fig. 2.8 shows the mean value and standard deviation of the Gaussian distribution for each material and highlights the values that correspond to the most desirable membrane performance. The black circles correspond to parameters with permeabilities more than twice that of Zr$_{54}$Cu$_{46}$ at 600 K, which could be targeted for materials development. Fig. 2.8 predicts that Zr$_{30}$Cu$_{60}$Ti$_{10}$ (T=Sc, Ta, Y, Ti) will have the best permeabilities for H$_2$, and that materials outside the rectangle in Fig. 2.8 will have highly unfavorable performance. An interesting feature of Fig. 2.8 is that it suggests that amorphous materials with optimized Gaussian distributions of binding energies will have permeabilities ~3 times that of pure Pd. This is likely to define an upper limit for H$_2$ permeability in amorphous metals.

In summary, DFT is useful for predicting the performance of metal-based materials for hydrogen applications because it describes key quantities like binding energies and heats of formation with sufficient accuracy and with, critically, no experimental input. Predictions of materials performance can be made for materials with compositions that span the periodic table provided that the DFT-based method meets the four other criteria for useful theoretical predictions presented in the Introduction. We have discussed several examples of our efforts to computationally screen either libraries of existing materials or proposed materials to identify systems with enhanced properties. Examples included substitutionally-disordered metal alloys, ordered stoichiometric compounds, and amorphous metals. Often in these screening studies, only a handful of many materials tested show potential for a given application. Without guiding principles to facilitate this down-selection, it would be a daunting task to pick winners a priori.

Tools that enable large scale DFT-based screening methods include easily navigable experimental crystal structure databases that are continually updated with completely solved structures and information on synthesis temperatures and pressures. Also, databases such as the Materials Project based on common DFT calculations that can be mined quickly to obtain DFT-optimized structures, ground state energies, electronic properties, or convex hulls will become important for efficiently evaluating materials for novel applications. Open source codes such as Pymatgen or AFlow that allow for automating property prediction algorithms also play an enabling role in increasing the number of calculations that can be completed using existing resources. Great strides are being made in the area of computational materials discovery and experimental-computational structure refinement that expand, complete, and improve current databases of both stable and metastable states. However, for continued acceleration in materials discovery and property prediction, we need methods that overcome DFT simulation size restrictions and rapidly explore potential energy surfaces to isolate stable structures of complex materials and transition states.
2.4.2 First principles methods for elpasolite halide crystal structure prediction at finite temperatures

We compared the performance of three levels of theory for four elpasolite halides, Cs$_2$NaGdBr$_6$, Cs$_2$NaLaBr$_6$, Cs$_2$LiLaI$_6$, and Cs$_2$LiScI$_6$, in order to determine the minimum level of theory required to accurately predict the equilibrium crystal structures at finite temperatures. We evaluate ground state, simple harmonic, and quasiharmonic free energies for each material in the common cubic, tetragonal, and trigonal symmetries using Density Functional Theory (DFT) and phonon calculations. The highest level of theory based on a quasiharmonic model accounting for thermal expansion reproduces available experimental phase information for the studied materials and outperforms the simple harmonic model. As expected, ground state energies alone do not provide unambiguous information regarding expected finite temperature crystal structures and fail to identify interesting materials that crystallize with cubic symmetry. The methods we demonstrate will be useful for considering the large number of elpasolite halides that exist to identify desirable crystal structures.

At a given temperature, the thermodynamically-preferred phase is that with the lowest Gibbs free energy as given by

$$G = U - TS + PV = F + PV,$$

where $U$, $S$, and $F$ are the internal energy, entropy, and Helmholtz free energy contributions, respectively.\(^\text{19}\) In our calculations the external pressure $P$ was zero so the quantity calculated was $G = F$, henceforth referred to as the free energy. Three approximations to $F$ with varying computational complexities were utilized. The simplest ground state model is described by

$$F(V_0) = E_0(V_0),$$

with $E_0(V_0)$ as the DFT electronic total energy at 0 K computed at the ground state volume $V_0$. This model ignores vibrational contributions to the free energy and cannot explicitly predict temperature-dependent phase transitions. The next level of theory, the simple harmonic model, is given by

$$F(V_0, T) = E_0(V_0) + F^{\text{vib}}(V_0, T)$$

and introduces temperature-dependencies through the vibrational free energy $F^{\text{vib}}$ evaluated at $V_0$. $F^{\text{vib}}(T)$ for a given volume was calculated via an integral over the vibrational density of states (VDOS). The direct method as implemented by Parlinski based on small displacements of non-equivalent atoms in the computational supercell was used to determine and integrate the VDOS, hereafter referred to as a phonon calculation.\(^\text{20}\) The computational cost of a simple harmonic model depends greatly on the degree of symmetry of the crystal structure, in particular the number of ion displacements required to compute the VDOS. The cubic, tetragonal, and trigonal symmetries studied in this work required 5, 11, and 21 displacements, respectively.

The third and highest level of theory applied is based on a quasiharmonic model in which the volume dependence of vibrational frequencies is taken into account:

$$F(V, T) = E_0(V) + F^{\text{vib}}(V, T).$$

In contrast to the simple harmonic model, which requires a single phonon calculation at $V_0$, the quasiharmonic model requires phonon calculations at multiple volumes to determine the free energy surface. At a given temperature, the volume that minimizes $F(V)$ is taken to be the equilibrium volume. Thus, thermal expansion of the solid is implicitly included. In this study, quasiharmonic calculations required an order of magnitude more computational effort than simple harmonic models.
Plane wave DFT calculations were performed using the Vienna \textit{ab initio} Simulation Package (VASP) with the projector augmented wave PW91 GGA exchange-correlation functional. 21 A cutoff energy of 500 eV was used for the plane wave basis set. Monkhorst-Pack \( k \)-point meshes were chosen to give approximately 0.028 Å\(^{-1} \) spacing along the reciprocal lattice vectors. First, geometry optimizations were performed on \( 1 \times 1 \times 1 \) unit cells of Cs\(_2\)NaGdBr\(_6\), Cs\(_2\)NaLaBr\(_6\), Cs\(_2\)LiLaI\(_6\), and Cs\(_2\)LiScI\(_6\) in the cubic (Fm-3m), tetragonal (I4-m), and trigonal (R-3m) orientations depicted in Figure 2.9. Volumes and ion positions were simultaneously relaxed until the Hellman-Feynman forces on each atom were less than \( 10^{-3} \) eV Å\(^{-1} \). Crystal structure stabilities based on computed DFT 0 K energies were then compared to remove high energy structures from further consideration for computational efficiency.

For each structure maintained for higher level consideration, volume-only stress minimization (static) quasiharmonic computations were completed, and final values for the ground state and simple harmonic models, Eq. (2.7) and Eq. (2.8), were derived from Eq. (2.9). Static quasiharmonic methods involve performing phonon calculations at each volume in a range of volumes for which the cell shape and ion positions have been simultaneously relaxed, i.e., the potential energy has been minimized. Between 8 and 15 volumes were used to parameterize \( F(V,T) \) for \( T \leq 500 \) K for all materials with the exception of Cs\(_2\)LiScI\(_6\), which was studied for \( T \leq 1000 \) K. Volume spacing ranged between 10 and 20 Å\(^3\) with the exception of Cs\(_2\)LiScI\(_6\), which employed a grid spacing of 5 Å\(^3\) close to the ground state volume and 20 Å\(^3\) at higher volumes to account for volume expansion at high temperatures. For each volume, cell shape and ion positions were relaxed until residual forces on each atom were less than \( 10^{-3} \) eV Å\(^{-1} \). Displacement magnitudes were chosen to yield significant maximum forces per atom in the range 0.5-0.8 eVÅ\(^{-1} \). For the direct method ion displacement force calculations, trigonal structures were transformed from the hexagonal setting used for initial geometry optimization to a rhombohedral orientation to best approximate a spherical supercell shape. Where soft modes were observed, manifest as negative frequencies in the VDOS, the VDOS was assumed to be zero, and no further adjustment to the free energy was made.

At each temperature, \( F(V) \) in Eq. (2.9) was fit to a 4\(^{th}\) order polynomial using MATLAB. The corresponding quasiharmonic equilibrium volume was taken to be that for which \( dF(V)/dV=0 \) and \( d^2F(V)/dT^2 >0 \) with value greater than the smallest tested volume. This ensured that the predicted equilibrium volume corresponded to a minimum of the free energy curve in close proximity to the range of tested volumes. A similar method was used to locate \( V_0 \) at the minimum of \( E_0(V) \). This method neglects zero point energy shifts in the predicted ground state volume. For a given temperature, the values of the fitted \( F(V) \) polynomial at the computed quasiharmonic equilibrium volume and at the fixed \( V_0 \) were taken to be the quasiharmonic and simple harmonic free energies, respectively.
Figure 2.9 Unit cells of elpasolite halide crystal structures with $A^+_2B^+B'^{3+}X^-$ stoichiometry: (a) cubic, (b) tetragonal, and (c) trigonal phases. Cages indicate $BX_6$ and $B'X_6$ octahedra.

The cubic, tetragonal, and trigonal crystal structures for $Cs_2LiScI_6$ were optimized using DFT to obtain ground state lattice properties and relative electronic energies. Table 2.1 presents the ground state energies from Eq. (2.6) in terms of relative energy per formula unit (f.u.). At this lowest level of theory based on DFT electronic energies alone, the trigonal phase is $0.162$ eV f.u$^{-1}$ ($0.160$ eV f.u$^{-1}$) more stable than the tetragonal (cubic) phase. Including zero point energies at the predicted ground state volumes does not change the predicted lowest energy structure at 0 K since the differences in zero point energy among the phases are less than $0.01$ eV f.u$^{-1}$. Including the zero point energy reverses the predicted relative stabilities of the metastable cubic and tetragonal phases due to the slightly larger zero point energy of the cubic phase.

Experimentally, $Cs_2LiScI_6$ adopts a 2L $Cs_2LiGaF_6$ prototype ($P\bar{3}m1$ space group) trigonal structure at low temperature with a different stacking sequence than the 12L $Cs_2NaCrF_6$ prototype ($R\bar{3}m$ space group) trigonal structure applied in this work. DFT optimization of $Cs_2LiScI_6$ in the 2L trigonal geometry indicates that the 2L arrangement is $0.128$ eV f.u$^{-1}$ lower in energy than the 12L structure at 0 K, not including zero point energy corrections. Thus, DFT correctly predicts the low temperature trigonal geometry for this material. As previously discussed, DFT methods exist for crystal structure prediction, including database search methods that compare relative energies of all known crystal structures consistent with a given stoichiometry. However, since the aim of this work is to compare the relative performance of different levels of theory and for consistency, we present results for the 12L trigonal structure considered for each elpasolite halide studied.
Table 2.1 Lattice properties of Cs$_2$LiScI$_6$ at 0 K predicted using Eq. (2.7) and Eq. (2.8). $\Delta E_0$ is the DFT electronic energy of the indicated phase relative to that of the most stable phase.

<table>
<thead>
<tr>
<th></th>
<th>cubic</th>
<th>tetragonal</th>
<th>trigonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$ (Å$^3$ f.u$^{-1}$)</td>
<td>415.2</td>
<td>415.3</td>
<td>425.0</td>
</tr>
<tr>
<td>$a_0$ (Å)</td>
<td>11.843</td>
<td>8.362</td>
<td>8.388</td>
</tr>
<tr>
<td>$c_0$ (Å)</td>
<td>11.878</td>
<td>41.843</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_0$ (eV f.u$^{-1}$)</td>
<td>0.160</td>
<td>0.162</td>
<td>0.0</td>
</tr>
<tr>
<td>$F_{vib}$ (eV f.u$^{-1}$)</td>
<td>0.137</td>
<td>0.127</td>
<td>0.136</td>
</tr>
</tbody>
</table>

Figure 2.10 Simple harmonic free energies for Cs$_2$LiScI$_6$ crystal structures: (a) absolute free energies and (b) free energies relative to $F(V_0,T)$ of ground state trigonal phase.

Figure 2.10(a) displays the temperature-dependent free energies for the three crystal structures based on the simple harmonic level of theory, which takes into account harmonic vibrational effects at the ground state volume but does not capture thermal expansion. For clarity, Figure 2.10(b) shows the free energies relative to that of the ground state trigonal phase. Free energies computed at this level of theory predict that Cs$_2$LiScI$_6$ undergoes a phase transition from trigonal to cubic at $T = 685$ K. Above this temperature, inclusion of $F_{vib}(T)$ is sufficient to
overcome the 0.16 eV f.u\(^{-1}\) energy difference between the two phases at 0 K. Although, to our knowledge, there are no experimental data available regarding phase transitions in Cs\(_2\)LiScI\(_6\), elpasolite halides are known to undergo similar transitions to the high symmetry cubic phase, as previously mentioned.

Figure 2.11 presents the free energies of the tetragonal and cubic structures relative to the ground state trigonal phase based on the full quasiharmonic calculation from Eq. (2.9), the highest level of theory, which allows for volume expansion. The shaded regions depict uncertainties in the relative free energies due to polynomial fitting errors. The fitting error in the free energy of a crystal structure at a given temperature was taken to be

$$|F_{\text{fit}} - \min(F_{\text{data}})|,$$

where \(F_{\text{fit}}\) and \(F_{\text{data}}\) indicate the free energy from the interpolated polynomial fit as previously discussed and the lowest energy computed directly from the tested volumes. The quasiharmonic level of theory lowers the predicted trigonal to cubic phase transition to \(T=391 \pm 43\) K. While the free energy difference between the trigonal and cubic structure over the studied temperatures spanned a range of approximately 0.15 eV f.u\(^{-1}\) for the simple harmonic case, the quasiharmonic level of theory expanded this relative energy range to 0.15-0.5 eV f.u\(^{-1}\). In comparison, \(\Delta E_0\) was 0.160 eV f.u\(^{-1}\). Thus, for this material, the effect of the simple harmonic level theory on the free energy is just able to overcome the ground state energy difference whereas the quasiharmonic free energy change is considerably larger. The quasiharmonic model is valid only at temperatures not approaching the melting point. While specific information on the melting point of Cs\(_2\)LiScI\(_6\) is unavailable, melting temperatures of Cs\(_2\)NaLaI\(_6\), Cs\(_2\)NaLaBr\(_6\), Cs\(_2\)LiLaI\(_6\), and Cs\(_2\)LiLaBr\(_6\) fall between 749 K and 868 K. Assuming that this range is a reasonable proxy for Cs\(_2\)LiScI\(_6\), the use of the quasiharmonic approximation in this case is justified since the predicted phase transition occurs well below the melting range.

Figure 2.11 Cs\(_2\)LiScI\(_6\) quasiharmonic free energies relative to \(F(V,T)\) of ground state trigonal crystal structure. Bounds indicate predicted uncertainties due to fitting.

Figure 2.12 shows the vibrational contribution to the free energy as a function of volume for Cs\(_2\)LiScI\(_6\) at 0 K and 300 K. For this system, the ground state volume is 415.2 Å\(^3\) f.u\(^{-1}\) based on minimization of \(E_0(V)\). The zero point energies display smooth and linear behavior over the tested volume range. However, \(F^{\text{vib}}(V)\) increasingly deviates from linearity for larger volumes.
with temperature. The vibrational entropy component of $F^{\text{vib}}$ of the extended volumes is responsible for the anomalous behavior. Conversely, $E_0(V)$ is largely smooth and parabolic. This behavior was observed with varying severity for all materials examined in this work with the exception of the tetragonal and trigonal phases of Cs$_2$NaGdBr$_6$ and Cs$_2$NaLaBr$_6$. These trigonal structures were not studied within the quasiharmonic approximation as previously discussed, and we cannot rule out the presence of linear deviations in the tetragonal phases at volumes greater than those studied.

Initially, only the composite free energies $F(V) = E_0(V) + F^{\text{vib}}(V)$ were curve-fit to find $F(T)$. To ensure that the instabilities in $F^{\text{vib}}(V)$ at larger volumes did not affect the predicted phase stabilities, we also computed quasiharmonic phase transitions using a linear fit of $F^{\text{vib}}(V)$ at each temperature for volumes in the small volume linear regime, i.e., volumes less than the onset of non-linear behavior, followed by extrapolation to the excluded volumes. For Cs$_2$NaLaBr$_6$, Cs$_2$NaGdBr$_6$, and Cs$_2$LiScI$_6$, the linear fit method predicts the same phase transitions as shown in Table 2.2 though at slightly shifted temperatures. The linear fit does not stabilize an otherwise high energy phase. For Cs$_2$LiLaI$_6$, the linear fit of $F^{\text{vib}}(V)$ stabilizes the cubic phase relative to the trigonal phase at room temperature while the direct-use of $F^{\text{vib}}(V)$ without linear fitting predicts a phase transition within the curve-fitting error bar as previously discussed. This comparison indicates that while the relative stabilities of the phases are largely unaffected by the non-linear characteristics of $F^{\text{vib}}(V)$ for large volumes, more accurate methods may be needed to precisely resolve finite temperature free energies of close competing phases. Phase transition predictions based on the simple harmonic level of theory are, of course, not affected by vibrational properties of extended volumes.

![Figure 2.12](image-url) Comparison of volume-dependent vibrational contribution to free energy for Cs$_2$LiScI$_6$ at 0 K and 300 K.

In summary, Computational methods that can screen large materials libraries to identify cubic elpasolite halides or provide finite temperature stability information to experimentalists are desirable for scintillator materials discovery. We studied four elpasolite halides with three levels of theory based on DFT ground state, simple harmonic, and quasiharmonic free energies in common cubic, tetragonal, and trigonal symmetries to determine the minimum level of theory required to predict the finite temperature equilibrium phase. Candidate screening based on
ground state energies alone did not successfully identify materials that crystallize with cubic symmetry since the cubic structure was predicted to be metastable in all cases. The results also do not indicate a clear or consistent method for using ground state energies alone for materials screening.

The calculations do show, however, that *ab initio* methods that include finite temperature vibrational effects are capable of reproducing the low temperature phase transitions of elpasolite halides. The relatively computationally-expensive quasiharmonic model, which accounts for thermal expansion, outperformed the simple harmonic model. It produced results consistent with available experimental information while the simple harmonic model failed to predict a known low temperature tetragonal to cubic phase transition for Cs$_2$NaLaBr$_6$. However, the quasiharmonic calculation was unable to clearly differentiate between the phases in all cases. More accurate quasiharmonic calculations may be able to resolve these relative energies with higher fidelity.

2.4.3 First principles investigation of ternary and higher metal hydrides for high temperature tritium sequestration application

Although the thermodynamics of metal hydrides at low to moderate temperatures have been successfully described with Density Functional Theory (DFT) calculations using 0 K total energies and simple harmonic models, it is unclear if this approach is valid for hydrides that are stable at high temperatures. To aid development of computationally efficient methods, this paper uses DFT to explore the predicted stabilities of ZrH$_2$, HfH$_2$, TiH$_2$, LiH, and NaH with four levels of theory. We also investigate isotope effects to understand if these should be accounted for in screening of deuterated or tritiated materials. We show that calculations that account for vibrational corrections to the crystal lattice are not necessary to get an accurate description of relative stabilities of metal hydrides. The shifts in dissociation temperatures due to isotope substitutions are <50 K for all materials, with larger shifts for lighter materials, as expected. We show that accounting for vibrational effects due to isotope substitution in metal hydrides is unnecessary to accurately predict the relative stabilities of metal hydrides at high temperatures.

While the quasiharmonic and explicit anharmonic corrections to the quasiharmonic free energy levels of theory provide estimates of thermal expansion in solid phases that are unavailable through ground state or simple harmonic free energies alone, it is unclear as to how much incorporating this dependency changes $T_d$. To assess these effects, we compare predictions of $T_d$ for ZrH$_2$ using four levels of theory. First we determine the appropriate method for computing free energies within the quasiharmonic approximation for anisotropic Zr and ZrH$_2$.

The unit cells of Zr and ZrH$_2$ each have two degrees of freedom, $a$ and $c$. Formally, $F(a,c,T)$, but the full search method, which varies each lattice parameter independently and computes the vibrational free energy for each configuration, requires much more computational effort than a static quasiharmonic calculation. Presumably, predictions of $a(T)$, $c(T)$, and $F(T)$ within the quasiharmonic approximation using the full search method are more accurate than those predicted via the static method. However, the full calculation required six times as many phonon calculations as the static treatment of the free energy based on the lattice grid sampling used in this work. Table 2.2 presents the lattice properties of Zr and ZrH$_2$ determined using both quasiharmonic methods along with comparisons to published experimental and first principles
results. For both Zr and ZrH₂ the full and static methods produce nearly identical ground state
values for $a$, $c$, $V$, and the bulk modulus $B$ where \(^{23}\)

$$B = V \frac{\partial^2 F(V)}{\partial V^2}$$  \hspace{1cm} (2.11)

The DFT results are within 2% of the experimental values for both Zr and ZrH₂, but
accounting for thermal expansion does not bring the predicted values into better agreement with
experimental values at 298 K.

Table 2.2 Lattice properties of hcp Zr and fct ZrH₂ at 0 K (298 K) predicted within the
quasiharmonic approximation using both full search and volume-only (static) stress minimization
methods.

<table>
<thead>
<tr>
<th></th>
<th>Zr</th>
<th>ZrH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
</tr>
<tr>
<td>Full</td>
<td>3.230</td>
<td>5.175</td>
</tr>
<tr>
<td></td>
<td>(3.235)</td>
<td>(5.180)</td>
</tr>
<tr>
<td>Static</td>
<td>3.231</td>
<td>5.174</td>
</tr>
<tr>
<td></td>
<td>(3.235)</td>
<td>(5.180)</td>
</tr>
<tr>
<td>Experiment</td>
<td>3.227(^a)</td>
<td>5.137(^a)</td>
</tr>
</tbody>
</table>

\(^a\) at 298 K, \(^b\),\(^c\) at 4 K and 298 K, \(^d\) at 297 K.

Figure 2.13 shows the predicted lattice expansion and isotropic volume thermal
expansion $\varepsilon$

$$\varepsilon = \frac{V - V_{\text{ref}}}{3V_{\text{ref}}}$$  \hspace{1cm} (2.11)

for Zr and ZrH₂ using the full search and static quasiharmonic methods where $V_{\text{ref}}$ is the volume
at a reference temperature. This definition is consistent with \(^{24}\) and \(^{25}\). For both Zr and ZrH₂,
static calculations predict similar rates of expansion in $a$ and $c$ while using the full search
method, $a$ is largely held constant with increasing temperature and expansion in $c$ drives the
overall unit cell volume expansion. Skinner and Johnston calculate $\varepsilon = 0.0051$ at 950 K with
$V_{\text{ref}} = V_{298}$ based on x-ray diffraction measurements of Zr lattice parameters. In comparison, our
calculations give $\varepsilon = 0.0039$ and $\varepsilon = 0.0045$ for the full and static methods, respectively, which
indicate reasonable agreement with the experimental result. Skinner and Johnston also determine
the average linear coefficient of expansion between 298 K and 1143 K as $5.5 \times 10^{-6}$ K\(^{-1}\) and
$10.8 \times 10^{-6}$ K\(^{-1}\) for $a$ and $c$, respectively. Our full search method gives $3.0 \times 10^{-6}$ K\(^{-1}\) and $12.0 \times 10^{-6}$
K\(^{-1}\) for $a$ and $c$, respectively, for the same temperature range. The static calculation predicts
$7.7 \times 10^{-6}$ K\(^{-1}\) and $5.6 \times 10^{-6}$ K\(^{-1}\) for $a$ and $c$, respectively. Based on this result, the full search
method more accurately predicts the anisotropic thermal expansion of Zr. Over the temperature
range studied, the lattice parameters for Zr expand only 0.01 Å in $a$ and 0.11 Å in $c$, which are on
the same order as the grid spacing we used to sample lattice configurations for the full method. A
more detailed study of the anisotropic thermal expansion of Zr would need to use finer grid
spacing. Nie and Xie similarly used DFT to study the thermal expansion of hcp Zr using a full search quasiharmonic method. While our predicted $\varepsilon$ with $V_{\text{ref}}=V_{293}$ are in good quantitative agreement, the predicted lattice parameter expansions agree only qualitatively. Our calculations predict slightly less expansion in $a$ and more expansion in $c$ than Nie and Xie. However, this may be due to differences in grid spacing.

The full search and static quasiharmonic calculations predict virtually identical volumetric thermal expansion for ZrH$_2$. Yakel studied the thermal expansion of ZrH$_{1.92}$ using x-ray diffraction and found that the linear coefficient of volumetric expansion based on the fct unit cell was $9.03 \times 10^{-6}$ K$^{-1}$ between 300 K and 700 K. Our calculations are in excellent agreement with an average linear coefficient of volumetric expansion over the same temperature range of $10.0 \times 10^{-6}$ K$^{-1}$ and $9.6 \times 10^{-6}$ K$^{-1}$ for the full and static methods, respectively. In Yakel’s work, $a$ contracts slightly by about 0.01 Å and $c$ expands by approximately 0.1 Å between 100 K and 800 K. The grid spacing in this work, $\Delta a = 0.03$ Å and $\Delta c = 0.05$ Å, is too coarse to perform detailed comparisons of the anisotropic expansion for ZrH$_2$. Our calculations indicate, however, that $a$ tends to expand more slowly than $c$, and that the volume expansion is driven by changes in $c$.

Figure 2.13 Predicted lattice constants and volume thermal expansion of hcp Zr and fct ZrH$_2$ within the quasiharmonic approximation using the volume-only (static) stress minimization (solid curves) and full search (dashed curves) methods: (a) lattice constant parallel to principal axis, (b) lattice constant perpendicular to principal axis, (c) volumetric thermal expansivity relative to lattice volume at 293 K.

Figure 2.14 shows the slight correction in predicted ground state volume from 55.6 Å$^3$ to 57.0 Å$^3$ for ZrH$_2$ upon inclusion of zero point energies. The zero point energy lattice correction is even smaller for Zr, with a marginal expansion from 46.7 Å$^3$ to 46.8 Å$^3$. Figure 2.15 displays the computed anharmonic correction terms for Zr and ZrH$_2$. Incorporation of $F_{\text{anh}}$ tends to decrease...
the total free energy of ZrH₂ and increase the free energy of Zr. However, adjustments are less than 1 kJ mol⁻¹ H₂ between 0 K and 500 K, rising to about 5.0 kJ mol⁻¹ H₂ and -2.4 kJ mol⁻¹ H₂ for Zr and ZrH₂, respectively, at 1500 K. Calculating ΔG via Eq. (2.4) leads to a predicted T_d of 1159 K compared with 1129 K computed with quasiharmonic free energies alone. At this temperature, ΔF^anh contributes approximately only 4.5 kJ mol⁻¹ H₂ to ΔG. For ZrT₂, the magnitude of ΔF^anh at T_d is nearly the same as for the protiated material, and T_d similarly increases by 34 K relative to the T_d determined using only static quasiharmonic free energies.

Table 2.3 compiles the predicted T_d of ZrH₂ for 1 bar H₂ pressure for each of the four levels of theory studied in this work. For models based on ground state energies and simple harmonic calculations, two methods for each level of theory are presented. Of the models that include finite temperature vibrational effects, i.e., simple harmonic and higher, the difference between the lowest and highest level of theory is only about 50 K which corresponds to an energy difference of about 7 kJ mol⁻¹ H₂ based on ΔS ≈ 0.130 kJ K⁻¹ mol⁻¹ H₂. Alapati et al. calculated the enthalpy of formation for several metal hydride systems including MgH₂, LiH, CaH₂, AlH₃, Ca(AlH₄)₂, and LiBH₄ using both Ultrasoft Pseudopotentials and PAW methods with the PW91 functional. Based on these systems the differences in calculated enthalpy of formation for these two methods range from 0 to 5 kJ mol⁻¹ H₂. Similar calculations using the PAW method with PW91 and PBE functionals resulted in differences of 12 kJ mol⁻¹ H₂ for LiH and 10 kJ mol⁻¹ H₂ for MgH₂. Even larger differences are encountered when comparing USPP-PW91 and USPP-rPBE functionals. These results indicate that the predicted thermodynamic properties are more sensitive to the DFT functional than the level of theory used to include finite temperature vibrational effects.

Figure 2.14 The shift in the ZrH₂ equilibrium unit cell volume (V₀) at 0 K upon addition of the volume-dependent zero point energy (ZPE) correction to the DFT electronic energy (E₀).
The finite temperature models that include thermal expansion of the solid phases – quasiharmonic and the explicit anharmonic correction to the quasiharmonic free energies – exhibit only minor corrections to the simple harmonic models. In the case of the Zr-H system, the magnitude of the static quasiharmonic correction to the simple harmonic $F(V_0, 1000 \text{ K})$ for ZrH$_2$ and Zr is only 3 kJ mol$^{-1}$ H$_2$ and 0.2 kJ mol$^{-1}$ H$_2$, respectively. Thus, the thermal expansion correction is negligible for this system. There is very little difference between the models that account for vibrational contributions to the free energy because $\Delta G$ largely behaves as a linear function of a constant $\Delta H$ and $\Delta S$ beyond the very low temperature regime. The models based on ground state energies rely on the choice of a constant $\Delta S$. The good agreement between $T_d = 1154 \text{ K}$, predicted for ground state energies including zero point energies, and the highest level of theory including anharmonic corrections, $T_d = 1159 \text{ K}$, is due to the fortuitous use of $\Delta S \approx 0.130 \text{ kJ K}^{-1} \text{ mol}^{-1} \text{ H}_2$ recommended by Zuttel for all metal-hydrogen systems. The assumed value happens to be very close to that predicted for the anharmonic model with $\Delta S = 0.133 \text{ kJ K}^{-1} \text{ mol}^{-1} \text{ H}_2$ based on linear regression of $\Delta G$ between 500 K and 1500 K. However, $\Delta S$ has been shown to be as low as 0.097 kJ K$^{-1}$ mol$^{-1}$ H$_2$ for complex metal hydrides such as LiBH$_4$. Thus, use of the assumed $\Delta S \approx 0.130 \text{ kJ K}^{-1} \text{ mol}^{-1} \text{ H}_2$ in ground state models may not yield results in as good agreement with higher levels of theory in cases where the entropy of reaction is significantly different than the assumed value.

Alapati et al. found that $-20 < \Delta E_{\text{ZPE}}^* + E_{\text{ZPE}, \text{H}_2} < -10 \text{ kJ mol}^{-1} \text{ H}_2$ for over 300 metal hydride decomposition reactions including reactions in which the metal hydride is destabilized by another compound where * indicates the change over the solid phases. That is consistent with the finding for the Zr-H system studied here with computed $\Delta E_{\text{ZPE}}^* + E_{\text{ZPE}, \text{H}_2}$ of -16.9 kJ mol$^{-1}$ H$_2$. Thus, with $\Delta S \approx 0.130 \text{ kJ K}^{-1} \text{ mol}^{-1} \text{ H}_2$ the simplest calculation based only DFT ground state electronic energies can predict $T_d$ to within approximately 150 K of the more rigorous computation that includes zero point energies. This is supported by the results shown in Table 2.4 for all five metal hydrides studied.
Table 2.3 Predicted temperature of dehydrogenation and reaction enthalpy at 0 K for ZrH$_2$ predicted using four levels of theory ($V_0$ and $V_{0c}$ refer to ground state volumes not corrected and corrected for zero point vibrational effects, respectively).

<table>
<thead>
<tr>
<th>Model Description</th>
<th>$T_d$ (K)</th>
<th>$\Delta H_0$ (kJ mol$^{-1}$ H$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state energies at $V_0$ – Eq. (2.7)</td>
<td>1284</td>
<td>166.9</td>
</tr>
<tr>
<td>Ground state energies including zero point energies at $V_0$ – Eq. (2.8)</td>
<td>1154</td>
<td>150.0</td>
</tr>
<tr>
<td>Simple harmonic calculation at $V_0$ – Eq. (2.9)</td>
<td>1108</td>
<td>150.0</td>
</tr>
<tr>
<td>Simple harmonic calculation at $V_{0c}$ – Eq. (2.9)</td>
<td>1123</td>
<td>150.7</td>
</tr>
<tr>
<td>Quasiharmonic (static) – Eq. (2.9)</td>
<td>1129</td>
<td>150.7</td>
</tr>
<tr>
<td>Explicit anharmonic correction to quasiharmonic (static) free energy – Eq. (2.11)</td>
<td>1159</td>
<td>150.7</td>
</tr>
</tbody>
</table>

For the five metal hydrides studied in this work, the lowest level of theory predicts $T_d$ to within approximately 150 K of the more rigorous quasiharmonic predicted value with the largest differences apparent for the heavy metal hydrides. With the exception of HfH$_2$, for which no experimental data could be found, the models including vibrational effects are within 70 K of the experimental values, and the simplest model predicts $T_d$ to within 200 K of the experimental value. This suggests that material screening based on DFT calculations seeking to identify metal hydrides that are thermodynamically stable to the release of hydrogen at high temperatures could first screen a library of materials based on $E_0$ alone. As previously discussed, the simple harmonic and ground state energies including zero point vibration models require the same amount of computational effort with our method of computing vibrational energies.

For all materials tested, the quasiharmonic thermal expansion correction to the free energy was minor, and the zero point energy correction to the ground state volume shifted $\Delta H$ at 0 K by less than 1.5 kJ mol$^{-1}$ H$_2$. TiH$_2$, ZrH$_2$, HfH$_2$, and NaH each had differences in the predicted $T_d$ for the simple harmonic at the uncorrected ground state volume and the static quasiharmonic models of less than 30 K or 4 kJ mol$^{-1}$ H$_2$ with the approximation $\Delta S=0.130$ kJ K$^{-1}$ mol$^{-1}$ H$_2$. The largest difference between the quasiharmonic and simple harmonic calculations at the uncorrected ground state volume was less than 70 K or 9 kJ mol$^{-1}$ H$_2$ for LiH. The quasiharmonic approximation estimates the volume dependence of the vibrational frequency and, consequently, the volume expansion of the solid phases. LiH melts at 961 K, and above this temperature the appropriate phase system is a mixture of liquid LiH, liquid Li, and H$_2$ gas. The quasiharmonic approximation is not valid for temperatures approaching the melting point because anharmonic effects are no longer negligible. In this two liquid region, H$_2$ reaches a pressure of 1 atm (≈1 bar) at 1184 K. This is only slightly larger than the simple harmonic and quasiharmonic predicted values of 1053 K and 1118 K, respectively. Similarly, the predicted values of $T_d$ for NaH are reasonably close to the experimental value considering that Na melts at low temperature. The performance of the thermodynamic models used in this work in predicting dissociation temperatures for metal-hydrogen systems with solids that melt at temperatures lower than $T_d$ is due to the linear nature of $\Delta G$. 

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Table 2.4 $T_d$ (K) for metal hydrides predicted using both static quasiharmonic calculation of free energies and free energies based on ground state energies at volumes uncorrected for zero point energy vibrational effects with and without zero point energy. Published experimental values are included for comparison. $\Delta S=0.130 \text{ kJ K}^{-1} \text{ mol}^{-1} \text{H}_2$

<table>
<thead>
<tr>
<th>Quasiharmonic</th>
<th>$T_d = \frac{\Delta(E_0)}{\Delta S}$</th>
<th>$T_d = \frac{\Delta(E_0 + ZPE)}{\Delta S}$</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>1118</td>
<td>1124</td>
<td>1075</td>
</tr>
<tr>
<td>NaH</td>
<td>647</td>
<td>664</td>
<td>655</td>
</tr>
<tr>
<td>TiH$_2$</td>
<td>946</td>
<td>1088</td>
<td>941</td>
</tr>
<tr>
<td>ZrH$_2$</td>
<td>1129</td>
<td>1284</td>
<td>1154</td>
</tr>
<tr>
<td>HfH$_2$</td>
<td>1003</td>
<td>1140</td>
<td>1001</td>
</tr>
</tbody>
</table>

Isotope effects in metal hydrides arise due to differences in vibrational frequencies of hydrogen isotopes in a crystal lattice. Isotope effects are known to cause changes in equilibrium lattice constants and thermal conductivities, as well as shifts in phase transition temperatures.\(^{21,64}\) Zhernov and Inyushkin wrote a review article on changes in phonon modes due to isotope composition in crystals. They note that for a polyatomic crystal the frequency shift of a vibrational mode is inversely proportional to $M_{c}^{1/2}$, the average mass of the crystal, and proportional to the square of the modulus of the associated polarization vector.\(^{30}\) Thus, metal hydrides with heavier isotopes will have smaller vibrational contributions to the free energy.

Figure 2.16 compares the magnitudes of the $\Delta H$ and $\Delta(-TS)$ terms for protium relative to deuterium and tritium in the TiX$_2$ metal hydride system. A cutoff energy of 350 eV and 8×8×8 $k$-points for consistency was proposed as with Hu et al.\(^8\) Our calculations are similar to Hu et al. except for the use of PAW (GGA-PW91) rather than USPP (GGA-PW91). At low temperature, negative $(\Delta G_{H_2} - \Delta G_{D_2})$ and $(\Delta G_{H_2} - \Delta G_{T_2})$ indicate that the heavier isotopes are more thermodynamically stable to the pure metal and associated hydrogen gas species than TiH$_2$. The hydrogen pressures in equilibrium with the solid species are ranked TiT$_2$ < TiD$_2$ < TiH$_2$ at low temperature. Above 360 K and 390 K for the tritide and deuteride, respectively, the relative stability ranking changes such that TiH$_2$ < TiD$_2$ < TiT$_2$ in terms of hydrogen pressures. Wiswall and Reilly determined a similar crossover point experimentally at 445 K for VH$_2$ and VD$_2$.\(^{31}\) At 0 K, $\Delta H_{H_2} - \Delta H_X$ is dominated by the difference in zero point energies of the metal hydrides.

The quasiharmonic approximation corrects equilibrium volumes for lattice vibrations. The magnitude of the correction to the unit cell volume for various metal hydrides at 0 K due to isotopic mass is shown in Table 2.5. The volume changes are presented as percentages of the uncorrected volume. The magnitude of the zero point energy correction for a given metal hydride depends on the slope of the vibrational free energy curve $F_{qh}^{\text{th}}(V, 0 \text{ K})$ and the shape of $E_0(V)$. The correction magnitude decreases for heavier isotopes and similarly decreases for heavier metal atoms.
Figure 2.16 Temperature-dependent contributions of $\Delta H$ and $\Delta(-TS)$ to $\Delta G = \Delta H + \Delta(-TS)$ for isotope-substituted Ti$X_2$ ($X = D$ and $T$) relative to TiH$_2$ determined using a simple harmonic model of the free energy at the zero-point energy corrected ground state volume: (a) TiD$_2$ relative to TiH$_2$ and (b) TiT$_2$ relative to TiH$_2$

Table 2.5 Zero point energy correction to ground state volume of metal hydrides due to hydrogen isotope mass ($V_{0c} - V_0$) $V_0^{-1} \cdot 100\%$ where $V_{0c}$ and $V_0$ are the zero point energy corrected and uncorrected unit cell volumes at 0 K

<table>
<thead>
<tr>
<th>X=</th>
<th>H</th>
<th>D</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiX</td>
<td>6.4</td>
<td>5.1</td>
<td>4.5</td>
</tr>
<tr>
<td>NaX</td>
<td>4.7</td>
<td>3.6</td>
<td>3.1</td>
</tr>
<tr>
<td>TiX$_2$</td>
<td>3.2</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td>ZrX$_2$</td>
<td>2.5</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>HfX$_2$</td>
<td>2.5</td>
<td>1.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

For the NGNP application described in the Introduction, metal hydrides can be considered as potential tritium sequestration materials at elevated temperatures. We have already shown for Ti$X_2$ that heavier hydrogen isotopes destabilize metal hydrides above a critical temperature, but how much does this shift $T_d$ at 1 bar hydrogen pressure? Table 2.6 presents the predicted stabilities in terms of $T_d$ for each of the hydrogen isotope-substituted metal hydrides studied based on a simple harmonic calculation at $V_0$. The results of the simple harmonic calculation are very similar to those of the more computationally intensive quasiharmonic approximation with the largest differences for the lightest metals, and the order of the stabilities is unchanged using the lower level of theory. As expected, metal hydrides substituted with lighter hydrogen isotopes are more thermodynamically stable beyond low temperatures.
However, since $T_d$ of the protide is within 50 K of the deuteride and tritide for each of the materials studied, calculations simply based on protium are expected to yield an adequate description of the thermodynamic stability of metal hydrides for operation with tritium. This is useful because protiated metal hydrides have largely been the focus of both experimental and theoretical studies.

**Table 2.6** $T_d$ (K) for metal hydrides predicted via simple harmonic calculation at the uncorrected ground state volume.

<table>
<thead>
<tr>
<th>X=</th>
<th>H</th>
<th>D</th>
<th>T</th>
<th>$\Delta T_d$ (H-D)</th>
<th>$\Delta T_d$ (H-T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiX</td>
<td>1053</td>
<td>1029</td>
<td>1020</td>
<td>24</td>
<td>33</td>
</tr>
<tr>
<td>NaX</td>
<td>620</td>
<td>591</td>
<td>579</td>
<td>29</td>
<td>41</td>
</tr>
<tr>
<td>TiX$_2$</td>
<td>930</td>
<td>920</td>
<td>915</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>ZrX$_2$</td>
<td>1108</td>
<td>1094</td>
<td>1089</td>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td>HfX$_2$</td>
<td>986</td>
<td>974</td>
<td>969</td>
<td>12</td>
<td>17</td>
</tr>
</tbody>
</table>

### 2.4.3 Absorption of hydrogen and deuterium on zirconium metal

The absorption of hydrogen and deuterium on a pure zirconium sample at elevated temperatures has been determined. The material used for this study was a pure zirconium powder (100 mesh) that was dried under an inert gas stream to remove the pentanol and water stabilizers during chemical shipping and storage. Previous results (XRD, TGA, and RGA) have shown that the Zr material will absorb hydrogen or deuterium from a He gas stream at elevated temperatures ($600^\circ$C). The XRD and RGA analyses were only able to qualitatively demonstrate the capability of Zr to absorb hydrogen and deuterium at elevated temperatures. TGA is required for quantitative analysis of the amount of hydrogen (or deuterium) absorption into the Zr metal alloy. The initial TGA analysis indicated that the amount of absorbed hydrogen was significantly higher than the calculated amount of absorbed gas based on the flow rates and absorption time. It was suspected that there was residual moisture or hydrocarbon species remaining on the sample even after the rigorous drying process. These chemical species would be expected to desorb at the elevated temperatures of the TGA analysis (up to $950^\circ$C). The residual gas analysis obtained as the temperature was increased during the TGA is shown below in Figure 2.17.
Figure 2.17 RGA of pure Zr during TGA heatup

Figure 2.18 RGA of deuterated Zr during TGA heatup

Figure 2.17 represents a sample of Zr material after the initial drying process but not subjected to the initial drying at 650°C as the absorption samples were. There is clear evidence of various species desorbing throughout the temperature range indicative of residual organic removal. Figure 2.18 shows a similar residual gas analysis obtained during the TGA temperature ramp, with a Zr sample that was deuterated (exposed to D₂ instead of H₂). Prior to deuterium absorption the sample was heated to 650°C in order to activate the material. This initial activation of the Zr material removed all of the pentanol intermediate species and only traces of water remained on the Zr surface. The TGA results of the deuterated Zr sample at present are inconclusive as there was no change in the mass of the Zr sample. However, even though the TGA results were inconclusive, we can conclude that at the temperature tested (600°C) that the maximum amount of hydrogen (or deuterium) that can be absorbed on the Zr sample is an H/M loading of 1.6 (moles of H atoms per moles of metal atoms). At 600°C the equilibrium pressure of H₂ absorbed on Zr is roughly 1 torr for a loading of 1.6 and the partial pressure of H₂ in the gas stream is 8 torr (1% H₂ in He at 800 torr). The maximum loading of Zr is an H/M of 2.0 and
the equilibrium pressure at this loading at 600°C is 100 torr. Given that the equilibrium pressure is higher than the H₂ pressure in the gas stream the maximum loading of H₂ cannot be reached under our test conditions which simulate actual hydrogen removal from He gas streams in NGNP applications. The experimentally determined equilibrium pressure of H₂ and D₂ absorbed on Zr under dilute He/H₂ mixtures in this work can be used to in potential future work on engineered systems for hydrogen isotope capture in NGNP systems.

2.4.4 Novel Ba₃Ca₁.1₈Nb₁.₈₂O₉₋δ based high temperature proton conducting ceramic

Compared to simple perovskite proton conductors, the complex perovskites may also show proton conduction given the appropriate degree of oxygen nonstoichiometry. In the complex perovskites, the B sites are usually occupied by ions from two or more different elements and can be categorized by the differences in the valences of the B site cations. The first category of these complex perovskites is a double perovskite with A₂(B'B")O₆ perovskite structure. In this case the B' and B" ions have valences 3+ and 5+, respectively. In the second category, B' and B" ions are 2+ and 5+, respectively, forming A₃(B'B")₂O₉ triple perovskite. Among the complex perovskites, Ba₃Ca₁.1₈Nb₁.₈₂O₉₋δ (BCN18), in which Ca²⁺ and Nb⁵⁺ ions are taken off stoichiometry by 18% (in opposite directions) to create negatively charged defects with which oxygen vacancies and/or protons can compensate, has been demonstrated almost pure proton conduction in reducing atmospheres. Further, BCN18 has shown remarkable chemical stability in CO₂ and water vapor environment at elevated temperatures. However, these impressive characteristics have not attracted too much attention because the relatively low conductivity hinders its practical applications where high proton conductivity is typically required.

The objective of the current work is to improve the conductivity of BCN18 proton conductor while retaining its chemical stability. As it is known that the choice of 1.18 for Ca sites is based on the ordering structure of B-site ions: when the ratio of Ca²⁺ reaches 1.18, the B-sites ions are more randomly distributed, which is more favored on conductivity compared with pure Ba₃CaNb₂O₉. In this study we are exploring B sites doping for BCN18 with Ce⁴⁺ (0.87 Å), which has smaller ionic radius than Ca²⁺ (1.00 Å) but larger ionic radius than Nb⁵⁺ (0.64 Å), in order to further decrease the B sites ordering status as well as change the concentration of the oxygen vacancies for a more favored electrical conductivity. The B sites nonstoichiometry of Ba₃Ca₁.1₈Nb₁.₈₂O₉₋δ (BCN18) is maintained at Ca 18% off, by doping different amount of Ce ions into either the B' or B" sites of BCN18, namely Ba₃Ca₁.₀₈Ce₀.₁Nb₁.₈₂O₉₋δ (B(CC0.1)N), Ba₃Ca₁.₁₈Nb₁.₇₂Ce₀.₁O₉₋δ (BC(NC0.1)), and Ba₃Ca₁.₁₈Nb₁.₆₂Ce₀.₂O₉₋δ (BC(NC0.2), aiming at enhancing the disordering status while changing the concentration of the oxygen vacancies in the material.

Figure 2.19 shows the XRD patterns of the samples sintered at 1550°C for 5 h. Single cubic complex perovskite structure with no secondary phases are obtained for all the samples, showing that BaCeO₃ has reacted with the nonstoichiometric perovskite phase completely. The small (111) peaks at 20 angle around 18.2° is an indication of B site 1:1 ordering of the perovskite structure for all the samples (shown in Figure 2.19 inset for the (111) step scan). The lattice parameters for the samples are 8.4095, 8.4149, 8.433 and 8.442 Å for BCN18, B(CC0.1)N, BC(NC0.1) and BC(NC0.2), respectively, consistent with step scan results of (220) peaks which shows a peak shift to a lower 20 degree (shown in Fig. 2.19 inset). For pure BCN18, it is B site 1:1 ordering mixed with random ordering. The introduction of Ce⁴⁺ (0.87 Å) into either Ca²⁺ (1.00 Å) sites or Nb⁵⁺ (0.64 Å) sites would promote the B-sites-disordering of the
structure, which would be expected to increase the ion mobility and consequently enhance the ionic conductivity\textsuperscript{39}. However, for sample B(CC0.1)N, a decrease in lattice parameter, with expectation of Ce\textsuperscript{4+} (0.87 Å) substitution on Ca\textsuperscript{2+} (1.00 Å), has not been observed. The increase of the lattice parameter may probably be due to the valence change of Ce\textsuperscript{3+} ions into Ce\textsuperscript{3+} ions (1.01 Å) for charge compensation consideration. Ce\textsuperscript{3+} is more likely to substitute into Ca\textsuperscript{2+} site because its ionic radius is more closely matched to that of Ca\textsuperscript{2+}. This will in turn deteriorate the disordering status of BCN18 structure and results in a decreased conductivity. For BC(NC0.1) and BC(NC0.2) samples, it is consistent with the expectation that the increase in the lattice parameters is a consequence of large Ce ions (either 3+ or 4+ oxidation states) substituted into small Nb\textsuperscript{5+} sites and an enhancement of the conductivity has been observed.

![XRD patterns](image)

**Figure 2.19** XRD patterns of samples sintered at 1550\textdegree C for 5 h, with step scan of (111) and (220) peaks in the inset pictures.

To further determine the Ce-ions’ oxidation states because of the doping effect, XPS measurements were employed to obtain the Ce 3d spectra for sample B(CC0.1)N and BC(NC0.1) shown in Figure 2.20. The Ce 3d spectra for CeO\textsubscript{2} and BaCe\textsubscript{0.85}Y\textsubscript{0.15}O\textsubscript{3-δ} (denoted as BCY) were also collected as references. It can be seen that for both B(CC0.1)N and BC(NC0.1) samples, the Ce-ions show a mixture of 3+ and 4+ oxidation states, indicating Ce\textsuperscript{3+} and Ce\textsuperscript{4+} ions co-exist for both samples. For example, for Ce-ions substituted into Nb\textsuperscript{5+} ions as supposed, there are Ce\textsuperscript{3+} ions that might either doped into Nb\textsuperscript{5+} or Ca\textsuperscript{2+} sites. Compared with B(CC0.1)N, the peak intensities for BC(NC0.1) are stronger at binding energy of 881 eV and 915.5 eV, which are characteristic of Ce\textsuperscript{4+} spectrum (starred peaks in Fig. 2.20)\textsuperscript{40}. This is indicative of more Ce\textsuperscript{4+} ions exhibited in BC(NC0.1) than in B(CC0.1)N. The XPS results confirmed with the XRD experiments that the Ca\textsuperscript{2+} sites are more favorable for Ce\textsuperscript{3+} substitution while smaller Nb\textsuperscript{5+} sites are more favorable for Ce\textsuperscript{4+} ions substitution. It is also noted that even for BaCe\textsubscript{0.85}Y\textsubscript{0.15}O\textsubscript{3-δ}, the Ce 3d spectrum shows a mixture of 3+ and 4+ oxidation states, probably because of the iconicity in perovskite structures with large covalent characteristics.\textsuperscript{41}
The microstructures of the sintered pellets are presented in Fig. 2.21. The top images reveal the surface morphologies while the bottom images are the corresponding cross-sectional view of the same samples. All the samples show dense microstructures, consistent with the Archimedes density tests that all the samples have greater than 94% relative densities. The average grain sizes measured from the surface images for the sintered pellets are 3.14±1.18, 2.41±0.90, 3.57±1.19 and 4.20±1.60 μm, respectively, indicating that the introduction of cerium into Ca$^{2+}$ sites will inhibit the grain growth, while the introduction of Ce ions into Nb$^{5+}$ sites will promote the grain growth and consequently reduce the density of grain boundaries. Therefore, the doping of Ce ions into either B’ or B’’ sites shows a clear effect on the grain growth of the sintered samples which would in turn affect the electrical performance.

The AC impedance spectra for the samples are conducted to measure the bulk and grain boundary conductivity of the samples. Typical Nyquist plots of the impedance spectra for sample BC(NC0.2) in wet air at 122 and 200°C are shown in Fig. 2.22 (a) and (b), respectively. The insets are the expanded views of the high frequency regions. The impedance spectra typically have three semi-circles corresponding to the bulk, grain boundary and electrode responses from high to low frequencies. As shown in the inset of Fig. 2.22(a) that at 122°C, a semicircle related to the bulk conduction process in the high frequency range (capacitance ~ $10^{-12}$ F cm$^{-1}$) can be clearly seen. With the temperature increased to 220°C, as shown in the inset of Fig. 2.22(b), only a portion of the semicircle corresponding to the bulk conduction response is observable in the high frequency range. When the temperature was further increased, the semicircle corresponding to the bulk conduction response can no longer be well defined and the bulk resistance can be then derived from the high frequency intercept of the intermediate frequency semicircle with the real axis. The semicircle in the intermediate frequency range is attributed to grain boundary responses (capacitance ~ $10^{-9}$ F cm$^{-1}$) while the spectrum in the low frequency range is due to the electrode response (capacitance ~ $10^{-4}$ F cm$^{-1}$). The other samples also have similar impedance spectrum evolution as a function of the testing temperature to that of BC(NC0.2).
Figure 2.21 SEM images of the sintered pellets; top images: surface morphology of the pellets; bottom images: cross-section view of the pellets.

Figure 2.22 Nyquist plots for BC(NC0.2) in wet air at (a) 122°C, and (b) 200°C. Inset pictures are expanded views of high frequency regions.

Fig. 2.23(a) and (b) show the total conductivities of the samples in wet air and wet H₂, respectively. It can be seen that the introduction of Ce ions into either Ca or Nb sites presents a distinct effect on the conduction behavior. Sample B(CC0.1)N shows the lowest conductivity among the different samples both in air and in H₂ at the same testing conditions. As discussed above in the XRD and XPS analysis, most Ce⁴⁺ ions may probably be reduced to Ce³⁺ ions to be substituted into Ca²⁺ sites. A decrease in the grain size has also been observed for B(CC0.1)N, resulting in an increase in grain boundary numbers and consequently an expected reduction in the total electrical conductivity. Another important factor that influences the electrical conductivity is the concentration of oxygen vacancies generated through doping. Substituting Ca²⁺ with either Ce⁴⁺ or Ce³⁺ will not lead to an increase of oxygen vacancies. Thus the decrease in conductivity for sample B(CC0.1)N can be viewed as a collective result of the above
correlations. As for samples BC(NC0.1) and BC(NC0.2), the electrical conductivity are increased compared with the undoped BCN18, with sample BC(NC0.2) showing the highest conductivity among the different samples tested at similar conditions (an enhancement of 78 % in electrical conductivity is achieved). Doping Ce ions (either Ce$^{4+}$ or Ce$^{3+}$) into Nb$^{5+}$ sites will result in an enhancement of the B-sites disordering and an increase in the concentration of oxygen vacancies. In addition, an increase in grain size has been observed for BC(NC0.1) and BC(NC0.2) compared with that of BCN18. All these factors are expected to lead to an increase in the electrical conductivity, which has been confirmed by the conductivity data.

Figure 2.23 Arrhenius plots of total conductivity for samples (a) in wet air, and (b) in wet H$_2$.

By separating the bulk and grain boundary conductivity, it is able to obtain detailed information on different contributions to the total conductivity. To evaluate the effect of introduction of Ce ions into Nb sites on the bulk and grain boundary conduction mechanisms, Fig. 2.24(a) and (b) show the Arrhenius plots of the bulk and grain boundary conductivity for samples BCN18 and BC(NC0.1) in wet air and wet H$_2$, respectively. Typically it is difficult to separate the grain boundary conductivity from the bulk conductivity when the testing temperature is high, however, in our experiments, because of the unique microstructure and characteristic of the BCN18 based samples, they can be separated up to 700$^\circ$C. In wet air the activation energies for BCN18 bulk, BC(NC0.1) bulk, BCN18 grain boundary, and BC(NC0.1) grain boundary conduction are 0.53, 0.463, 1.10, and 1.12 eV, respectively, showing almost linear behavior in Arrhenius plots. In wet H$_2$ at temperatures below 550$^\circ$C, for bulk conduction, the activation energies for BCN18 and BC(NC0.1) are 0.57 and 0.55 eV, respectively. While at elevated temperatures higher than 550$^\circ$C, a decrease in activation energy for bulk conduction is clearly observed, with activation energy of 0.13 and 0.1 eV, respectively, characteristic of electronic conduction. It should be noted that the slope change of the bulk conduction proceeds gradually while there is little change for that of the grain boundary conduction. The activation energies for grain boundary conductivity are 0.88 and 0.89 eV for BCN18 and BC(NC0.1), respectively. Therefore, it can be concluded that the bowed behavior of the total conductivity plot above 550$^\circ$C is mainly attributed to the change in the mechanism of the bulk conduction.
To evaluate the chemical stability of Ce doped BCN18 materials, the sintered pellets were exposed into boiling water and CO$_2$ atmosphere at elevated temperatures. Fig. 2.25(a) shows the XRD patterns of the pellets after boiling in water for 7 h. It can be seen that after boiling in water for 7 h, all the samples maintain pure perovskite structure with no detectable impurity phases. It is noticed that the peak intensity decreased after the treatment, especially for sample BC(NC0.2). This may be caused by the absorption of H$_2$O in the samples during treatment. FTIR spectrum study also confirmed the water adsorption on boiled Ba$_3$CaNb$_{1.75}$Ti$_{0.25}$O$_9$-$\delta$ samples as reported by Thangadurai.$^{44}$

The stability tests were also conducted in CO$_2$ atmosphere at 700°C for 4 h as well as in wet 3 vol% CO$_2$ (air as the balance gas, 3 vol% H$_2$O) at 700°C for 24 h, both with a flow rate of 50 mL min$^{-1}$ to evaluate the stability in carbon dioxide environments. XRD patterns of the samples after exposures are presented in Fig. 2.25(b) and (c), respectively. It can be seen that no impurity phases have been detected for the samples treated in CO$_2$ environment, suggesting no reaction taken place between CO$_2$ and the samples. Inspection of the samples after treatments revealed no apparent change in either color or morphology of the samples, consistent with the XRD results. Consequently, the introduction of Ce ions into either B’ site or B’’ site did not show any detrimental effect on the chemical stability for BCN18. Combined with the conductivity results, the doped BCN18 system turns to be a very promising intermediate temperature proton conductors, with respect to the stability tests mentioned above for Ba(Ce,Zr)O$_3$ based simple perovskite systems.
2.4.5 Microstructure modification of BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ and Ba$_3$Ca$_{1.18}$Nb$_{1.82}$O$_{9-\delta}$ based proton conducting ceramics

It is widely known that microstructure of the ceramics has significant impact on the performances. In many cases the mechanical and electrical properties can be readily modified just by altering the grain size distributions without changing the compositions of the ceramics$^{45,46}$. Many parameters, such as particle sizes of the reactant materials, fabrication methods, and even the microstructure of the green bodies will affect the final microstructures of the sintered ceramics. In addition, the choice of sintering profiles plays a crucial role to adjust the final microstructure, especially the grain size distributions and densities of the ceramics. As a promising alternative to prepare fine microstructured dense ceramics, the recently developed two-step sintering method has been proved to be less costly and more efficient.$^{48}$

Powder samples of doped barium cerates having the nominal composition of BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ (BZCYYb) were synthesized by a co-precipitation method as reported previously [10]. The pressed pellets after calcination at 1100 °C were sintered by a two-step sintering method in which the samples were heated at 5°C min$^{-1}$ to 600°C and held for 2 h to remove the organic PVA bonder, followed by heating at a rate of 5°C min$^{-1}$ to a peak temperature at 1450°C and held for 1 min to achieve an intermediate density, then cooled at 15°C min$^{-1}$ to
1300°C and held for 20 h, during which the ceramic densification was achieved while grain growth was suppressed. The sintering profile is shown in Fig. 2.26. As comparison, some pressed pellets were sintered by a conventional sintering method in which the pellets were heated to 600°C and held for 2 h, followed by heating to 1450°C at a heating rate of 5°C min⁻¹ and held for 5 h. Some co-precipitate raw powders were also pressed directly into pellets and sintered through a reactive sintering method in which the pellets were heated to 600°C and held for 2 h, followed by heating to 1450°C at a heating rate of 5°C min⁻¹ and held for 5 h, where the decomposition of the co-precipitate to form perovskite phase and subsequent sintering of the perovskite powders took place consecutively. The sintered pellets are named as Two-step, Conv., Reactive for samples sintered via two-step sintering method, conventional sintering method, and reactive sintering method, respectively.

![Figure 2.26](image)

**Figure 2.26** Two-step sintering profile for BZCYYb ceramic.

Fig. 2.27 shows the TEM bright field image of BZCYYb co-precipitated raw particles. Fig. 2.27 inset is the FESEM morphology of particles of the raw powder. It can be seen that fine particles with an average particle size around 30 nm are loosely agglomerated. The co-precipitation method adopted here produces spherical and uniform nano-sized grains, which is advantageous for the decomposition to form BZCYYb phase and the subsequent densification of the BZCYYb ceramics.

![Figure 2.27](image)

**Figure 2.27** TEM bright filed image of BZCYYb raw powder prepared by co-precipitation method. Inset is the FESEM picture of the powder.
Fig. 2.28 are the XRD patterns of the sintered pellets using different sintering methods. All the samples show predominantly orthorhombic perovskite structure similar to that of BaCeO$_3$ (JCPDS No. 22-0074). Since Y$^{3+}$ (0.9 Å) and Yb$^{3+}$ (0.868 Å) have similar ionic radii to that of Ce$^{4+}$ (0.87 Å), a solid solution is expected to form by doping Y and Yb into Ce sites. Trace amount of (Y, Ce)O$_{2-\delta}$ impurity peaks was found in the conventional and reactive sintered samples. It was noted that there was (Y, Ce)O$_{2-\delta}$ impurity for both two-step sintered and conventional sintered samples after calcined at 1100°C for 5 h. While after sintering, for the sample sintered via two-step sintering method, there was less impurity existed and thus was hard to discern by XRD. Based on the difference of the sintering profiles, the possible reason is that the (Y, Ce)O$_{2-\delta}$ dissolved into the lattice during the second holding stage for the two-step sintered samples. It is possible that (Y, Ce)O$_{2-\delta}$ diffuses and dissolves into the lattice with the grain boundary diffusion during the prolonged holding period at the second-stage with lower sintering temperature. The prolonged holding time is also beneficial for a higher solubility for the dopants and thus can be viewed as a homogenization process. For conventional sintered and reactive sintered samples, the diffusion energy for the grain boundary is not met while the activation energy for grain boundary migration (grain growth) is guaranteed, leading to the segregation of the impurities in the grain boundaries. In addition, for conventional and reactive sintered samples, the possible Ba loss during high temperature sintering might also promote the formation of (Y, Ce)O$_{2-\delta}$ impurities.

Figure 2.28 XRD patterns of the sintered BZCYYb samples via conventional sintering method (Conv.), reactive sintering method (Reactive) and two step sintering method (Two-step).

Fig. 2.29(A-C) are the surface while Fig. 2.29(a-c) are the cross-sectional FESEM images of BZCYYb samples sintered via conventional sintering, reactive sintering, and two-step sintering, respectively. It can be seen that all the samples are well sintered with sub-micron grain sizes. Two-step sintered BZCYYb sample shows the finest grain size of 184 nm and a porosity of 3.13% measured by mercury porosimetry, compared with that of 445 nm with a porosity of 1.91% for conventional sintered sample. The difference in grain sizes is a clear indication that the activation energy for grain boundary migration is not satisfied while the grain boundary diffusion is active for BZCYYb by the two-step sintering profile.

The sintering behaviors of the samples were investigated by the dilatometry. Calcined samples were pressed into cylinders and sintered via two-step sintering and conventional
sintering methods in the dilatometer. For reactive sintered samples, the raw powders were directly pressed into cylinders and measured by the dilatometer. Fig. 2.30 shows the dilatometric curves of BZCYYb samples with different sintering profiles. Inset is the expanded view of the linear shrinkage rate $dL/dt$. From the linear shrinkage curve $dL/L_0$ it can be seen that the sample from the reactive sintering method had the largest shrinkage during the sintering process. This is expected because in addition to the shrinkage at high temperature as a result of phase formation and densification process, considerable shrinkage took place at low temperature range (below 600°C) due to removal of absorbed water and decomposition of the carbonates. Both the conventional sintering and two-step sintering methods showed similar trend up to 1450°C since they have the same sintering profile prior to reaching 1450°C. After the sample reached 1450°C for 1 min, fast cooling rate helped prevent additional grain growth, thus enabling further shrinkage for two-step sintered sample, consistent with modeling prediction that relatively fast cooling rate is preferred for two-step sintering method\textsuperscript{52}. During this stage, the linear shrinkage percentage $(dL/L_0)$ increased from 18.2% for the conventional sintered samples to 19.4% for the two-step sintered ones. From the linear shrinkage rate shown in the inset, the maximum shrinkage rate $(dL/dt)_{\text{max}}$ occurred around 398 min (at 1370°C) for all the samples. A peak temperature of 1450°C as the first sintering step is appropriate for the two-step sintered BZCYYb samples, since an intermediate density higher than 70% is necessary to guarantee the disappearance of supercritical pores while the other pores become subcritical and unstable against shrinkage to ensure a subsequent densified body at a lower holding temperature at 1300°C.

Figure 2.29 FESEM pictures of BZCYYb sample pellets sintered via different profiles. Left: Surface morphologies; Right: Cross-sectional morphology; (A,a) Conventional; (B,b) Reactive; (C,c) Two-step.
Fig. 2.31 presents the Arrhenius plot of the conductivity for BZCYYb in wet air and wet hydrogen, respectively. The activation energy can be calculated through the Arrhenius equation

$$\sigma T = A \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (2.12)

where $A$ is the pre-exponential factor proportional to the charge carrier concentration, and $E_a$ is the activation energy associated with the transport mechanism and can be calculated from the slopes in Fig. 2.31. The defect chemistry for proton conduction can be described as

\[ H_2O(g) + O^\bullet_o + V^\bullet^\circ_o = 2OH^\circ_o \]  \hspace{1cm} (2.13)

where $O^\circ_o$ represents oxygen lattice, $V^\bullet^\circ_o$ denotes oxygen vacancy, and $OH^\circ_o$ represents proton charge carrier formed within the structure by attaching to the oxygen lattice. It can be seen in Fig. 2.31 that for all the samples, the activation energy in wet air is higher than that in wet $H_2$, indicative of different conducting mechanisms. In wet air, the proton conductors are believed to be mixed conduction with the oxygen ion conduction competing with the proton conduction.

In both air and $H_2$, the samples sintered by two-step sintering method show the highest conductivity, with $1.0 \times 10^{-2}$ and $1.4 \times 10^{-2}$ S cm$^{-1}$ at 600°C in wet air and wet $H_2$, respectively, followed by samples sintered via the reactive sintering method, while the samples sintered using the conventional sintering method have the lowest conductivity at the same testing conditions. The reason for the increase in conductivity may be attributed to the grain size effect on conductivity, and largely attributed to the improved grain boundary conductivity as a result from fewer amounts of impurity defects in the grain boundaries. The intrinsic grain boundary resistance may also play an important role to influence the grain boundary conductivity based on the space-charge model reported elsewhere.\textsuperscript{53, 54} It is noted the sample sintered by two-step sintering method shows similar conductivity compared with literature results\textsuperscript{55}, while the conventional sintered samples using powders prepared by a co-precipitation method exhibits lower conductivity compared with samples prepared by solid state reaction method and Pechini method,\textsuperscript{56} probably because of the secondary phases segregated in the grain boundaries which will deteriorate grain boundary conductivity and thus the total conductivity as reported in our previous study.\textsuperscript{40}
2.4.6 Novel chemically stable $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82-x}\text{Y}_x\text{O}_{9-\delta}$ proton conductor: improved proton conductivity through tailored cation ordering

Of the different types of proton conducting ceramics studied, simple perovskite structured rare-earth-doped alkaline earth based cerates (such as $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$) have attracted considerable attention due to their highest levels of proton conductivity. However, these cerates are readily decomposed in $\text{CO}_2$ and/or humid atmospheres at elevated temperatures due to their inherit thermodynamic instability under such conditions. Two strategies have been exploited to circumvent this problem. The first is to partially replace Ce ions with more electro-negative cations such as Zr in order to form a solid (Ce,Zr) solution and improve the chemical stability. Alkaline earth zirconates are much more stable, however the introduction of Zr into Ce site also greatly deteriorates the total conductivity. The alternative is to explore new proton conducting ceramics with good chemical stability while maintaining high proton conductivity. Several novel structured compounds have so far been reported as proton conducting oxides. Acceptor-doped $\text{LaNbO}_4$ based orthoniobates were reported to possess pure proton conductivity at temperatures below $700^\circ\text{C}$; $\beta$-$\text{K}_2\text{SO}_4$ structured $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-x/2}$ compounds containing GaO$_4$ tetrahedral units were found to possess significant proton conductivity although they were first discovered as fast oxide-ion conductors; perovskite related oxygen deficient brownmillerite structured $\text{Ba}_2\text{In}_2\text{O}_5$ demonstrated significant proton conductivity due to its intrinsic oxygen vacancies; and the cation off-stoichiometric complex perovskite structured $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ (BCN18) showed a proton transport number close to unity in reducing atmospheres. Although these novel structured compounds exhibited proton conduction at elevated temperatures, the proton conductivity values are unfortunately fairly low compared to the simple perovskite structured proton conductors. Nevertheless, some of the novel proton conductors possess unique properties. Among them, the complex perovskite structured BCN18 exhibits remarkable chemical and structural stability in $\text{CO}_2$ and/or water atmospheres. Consequently, if the proton conductivity of BCN18 can be improved without sacrificing its chemical stability, this material could present a breakthrough in searching for new proton conducting ceramics for important industrial applications.
Ba$_3$Ca$_{1.18}$Nb$_{1.82}$O$_{9-\delta}$ is originally derived from Ba$_3$CaNb$_2$O$_9$, in accordance with the complex perovskite structure $A_3B'B''_2O_9$, where 1/3 of the B sites are occupied by Ca$^{2+}$ ions, while the remaining 2/3 of the B sites are occupied by Nb$^{5+}$ ions. Stoichiometric Ba$_3$CaNb$_2$O$_9$ is 1:2 ordered for the B site cations, in which Ca$^{2+}$ and Nb$^{5+}$ ions are distributed on three planes, one plane primarily containing Ca$^{2+}$ and the other two planes primarily containing Nb$^{5+}$, where Ca$^{2+}$ and Nb$^{5+}$ cannot move freely from B’ to B” site or vice versa. Chart 1(a) shows the crystal structure of Ba$_3$CaNb$_2$O$_9$ with a P-3m1 space group. Pure Ba$_3$CaNb$_2$O$_9$ is an insulator since no oxygen vacancies are present in the structure. In addition, the B-site cation ordering blocks the movement of the ionic defects. The degree of ordering in the structure has dependence on the oxidation states and radii differences of the B site cations. Since the cations of Ba$_3$CaNb$_2$O$_9$ cannot move freely due to the ordering, the diffusion of the oxygen vacancies will also be limited due to the substitutional ordering on the cation sublattice (cation-vacancy ordering). To be a proton conductor, the formation of protonic defects should be created from the dissociative adsorption of water via eq. (2.13). In the presence of water vapor, the concentration of protonic defects and proton conductivity can be expected to increase with an increase in oxygen vacancy concentration. The introduction of Ca$^{2+}$ off-stoichiometry not only creates oxygen vacancies which support significant proton conductivity, but also modifies the B-sites ordering. In the off-stoichiometric BCN18 with Fm-3m space group, some of the B sites (4b) are occupied by ordered Nb$^{5+}$ while the remaining Ca$^{2+}$ and Nb$^{5+}$ ions are randomly distributed in 4a sites. The B-site ordering is still present in the double perovskite BCN18 due to the unevenly distributed B’ and B’’ sites (Fig. 2.32).

It is noteworthy that the amount of oxygen vacancies may further be increased by doping with aliovalent cations in the B-site. For example, a trivalent metal ion such as Y$^{3+}$ doped into Nb$^{5+}$ site would create an oxygen vacancy according to equation (2.14):

\[ Y_2O_3^{3+} \rightarrow 2Y^{3+} + 3O^{2-} + 2V'_o \]  

(2.14)

Besides the oxygen vacancy concentration, the B-sites ordering of the cations represents another factor that may influence the defect diffusions and thus the proton conductivity. Assuming that yttrium is doped into the B sites, the dopant Y$^{3+}$ with a coordination number of 6 has an ionic radius of 0.9 Å, which is situated between that of Ca$^{2+}$ (1.00 Å) and Nb$^{5+}$ (0.64 Å). The resulting small difference in ionic radius will favor a less ordered structure. From the tolerance factor t for the perovskites

\[ t = \frac{r_A + r_O}{\sqrt{2(r_{A+B''})}} \]  

(2.15)

where $r_A$, $r_O$ are the ionic radii of the A-site cation and oxygen anion, $r_{A+B''}$ is the average radii for B-site cation. For BCN18, t=0.973, indicating an almost cubic structure. The introduction of larger ionic sized Y$^{3+}$ (compared with Nb$^{5+}$) would distort the lattice parameters while still maintaining the perovskite structure as long as t>0.8. In fact, our structure refinement results indicate that introduction of Ca and Y in Ba$_3$Ca$_{1.18}$Nb$_{1.82-x}$Y$_x$O$_{9-\delta}$ leads to a Fm-3m structure (Shown in Fig. 2.32(b)). In this study, we evaluated the effect of partial substitution of Nb ions by different amount of Y ions on the crystal structure, oxygen vacancy content, ordering of the structure and electrical conductivity for the BCN18 system. These compositional modifications were aimed at improving the proton conductivity by introducing more oxygen vacancies and tuning the cation-ordering of the system without sacrificing the chemical stability.
Figure 2.32 (a) Crystal structure of rhombohedral $\text{Ba}_3\text{CaNb}_2\text{O}_9$ ($P-3m1$), and (b) cubic $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ ($Fm-3m$). Pink balls: Ba A-sites; Green balls: Nb-dominant B’’ sites; Blue balls: Ca rich B’ sites; O atoms are not shown here for clarity.

Fig. 2.33 (a-c) shows the Neutron powder diffraction patterns of BCN18, BCNY0.2 and BCNY0.3, respectively. These diffraction patterns can be indexed and refined based on the double-perovskite structured $Fm-3m$ as shown in Chart 1(b). According to the Rietveld refinement with trial and error, better agreement was found for the case that the $\text{Ca}^{2+}$ ions located at 4a sites (B’-site), rather than in 4b sites (B’’-site) while the $\text{Y}^{3+}$ ions distributed in both sides with exchange of $\text{Nb}^{5+}$ ions. The BCNY0.5 sample pellet showed secondary impurities on the surface. It was noticed that trace amount of $Fm-3m$ structured $\text{CaO}$ phase with lattice parameter of $a=4.81$ Å can be identified as the secondary phases in the Y doped samples by the high resolution neutron diffractions, although the impurity in BCNY0.2 and BCNY0.3 could hardly be detected by XRD. This is because the large neutron beam size and the large exposed sample volume make it possible to observe small amount of the secondary phase. Furthermore, the different neutron scattering coherent cross section of Ca (2.78 barn), Nb (6.253 barn), Y (7.55 barn) and O (4.232 barn) atoms is helpful to identify the locations and occupancies of these individual atoms, and thus to characterize the ordering structures. Selected structural parameters by Rietveld refinement are shown in Table 2.7. The lattice parameter increases with the yttrium doping level due to the larger yttrium dopants compared with the niobium ions. Sample BCNY0.2 leads to 0.325 wt% $\text{CaO}$ precipitation, while BCNY0.3 results in 0.963 wt% of $\text{CaO}$ precipitation. Although we intended to substitute Y on the Nb site, the Rietveld refinement suggested some of the doped Y may enter the Ca site resulting in trace amount of $\text{CaO}$ segregation. In consideration of the loss of Ca, the compositions of the samples are slightly adjusted apart from the nominal compositions, so that the Ca occupancy in B site accordingly matches the weight percentage of $\text{CaO}$ while the Nb/Y ratio is maintained. The atomic occupancies for selected samples are calculated and presented in Table 2.7. These results indicate that the substitution of $\text{Nb}^{5+}$ by $\text{Y}^{3+}/\text{Ca}^{2+}$ provides the required charge compensation from the difference in valences between $\text{Y}^{3+}/\text{Ca}^{2+}$ and $\text{Nb}^{5+}$. By trials and errors of the refinement, it is found that Ca will only stay in 4a site and not be allowed to be in 4b site. This result coincides with the large radii mismatch between $\text{Nb}^{5+}$ and $\text{Ca}^{2+}$, which is one of the reasons for the Ca/Nb ordering structure. Although not leading any exchange of $\text{Ca}^{2+}$ to 4b site, the occupancy of Nb at 4b site was decreased due to the introduction of Y, which moderated the disparity of 4a and 4b sites and reduced the B-site cation ordering. The oxygen occupancies for the materials are refined and presented in Table 2.7, oxygen vacancy numbers of 6.0%, 9.1%, and 8.9% for
BCN18, BCNY0.2 and BCNY0.3, respectively. It is noted that the actual increment of $V_\delta$ is not as anticipated from the formulated ones based on charge neutrality due to the trace amount of segregated CaO. Our XPS results also confirmed different oxidation states for Ca 3d spectra in the samples. It is also noted that the $V_\delta$ contents in BCNY0.2 and BCNY0.3 are similar. This is due to the fact that the introduction of more Y$^{3+}$ dopants into BCNY0.3 generated extra oxygen vacancies but more Ca$^{2+}$ loss balanced this effect. From the structure factor information, the presence of (111) and (311) peaks around 18 and 35 degree in XRD patterns are attributed to the non-identical scattering factors of the atoms at 4a and 4b sites, respectively. For the fully disordered perovskite, the cations at 4a and 4b sites are identical, and the (111) and (311) superlattice reflections will not be present. The intensity ratio for (111)/(220), (311)/(220) and (311)/(222) peaks can thus be indexed as the characteristics for the degree of B-site ordering in the perovskite structure. The peak intensity ratios of selected samples are presented in Table 2.8. It can be seen from Table 2.8 that as more Y$^{3+}$ dopant is added, the relative intensities of (111) and (311) peaks are decreased, indicating a lower degree of B-site cation ordering. This is expected since X-ray scattering factor is proportionally related to the atomic weight in the periodic table, and the scattering factor of Y is suited between that of Nb and Ca. The Y$^{3+}$ doping in 4a sites (which can substitute either Nb$^{5+}$ or Ca$^{2+}$) causes a reduction of the difference in the scattering ability between 4a and 4b sites. Fig. 2.33(d) shows the in-situ high temperature neutron diffraction 2D contour pattern for sample BCNY0.3 tested in vacuum furnace cooling from 1400°C down to 400°C at a cooling rate of 3°C min$^{-1}$. The brightness change of the pattern indicates the intensity change of the neutron diffraction peaks. It can be seen that upon reducing the temperature from 1400 to 400°C, there are only slight changes in peak intensities and d-spacing shifting due to Debye-Waller effect and thermal expansion, respectively. There is no apparent phase transformation for BCNY0.3 during the cooling process. In-situ high temperature XRD also confirmed no phase transformation from room temperature to 1000°C. It is believed that an oxygen atom forms two short bonds with B cations, and two long bonds with A cations in the perovskite, which means that an oxygen vacancy is more strongly trapped by a B'-O-B'' pair than by an A-O-A pair in $A(B'B'')_3O_3$ perovskite.$^{36}$ Consequently, substitution of Y for Nb perturbs or decreases the degree of ordering for oxygen vacancies in such a way that the oxygen vacancy is trapped by the Ca-O-Nb, Ca-O-Y, and Y-O-Nb pair. To check the crystal structure and the degree of cation ordering, the selected area electron diffraction (SAED) patterns and high resolution...
TEM (HRTEM) images were then collected for the sintered BCNY0.2 and BCNY0.3 powder samples shown in Fig. 2.34 and Fig. 2.35, respectively. The patterns have been indexed according to double perovskite structure-type cell and the lattice parameters were calculated based on the SAED patterns and TEM images. The SAED pattern of BCNY0.2 is characteristic of a typical cubic perovskite along the [111] zone axis of the sample aligned parallel to the electron beam, with calculated d(220)=0.2892 nm, consistent with the XRD and neutron powder diffraction results for the structural configuration of the sample. In addition to the Bragg reflections characteristic of the perovskite unit cell, superlattice reflections are observed (indexed by arrows in the pattern), indicating the presence of extra domains. The extra nano-domains have been confirmed by observing the corresponding HRTEM image and magnified areas shown in Fig. 2.34(iii) and Fig. 2.34(A-C). The chessboard and stripe typed patterns observed are attributed to the ordering in the structure, which may be caused by displacement of atoms, variation in the occupancy of atomic sites, or by both. In our case, it is mainly caused by the B-site cation ordering due to the differences in ionic radius and charges among the Ca$^{2+}$, Nb$^{5+}$ and Y$^{3+}$ ions. The SAED pattern along the [100] zone axis of BCNY0.3 shows no extra spots coexisting with the ideal perovskite unit cell. However, differences in brightness of the spots are indicative of a superlattice reflection due to the ordering of the structure.$^{37,38}$ The reconstruction of the reciprocal space from the SAED pattern leads to a superstructure of the cell, with $a' = \sqrt{2}/2a$ as shown in Fig. 2.35(A). The superstructure of the cell parameter is clearly observed on the HRTEM image by the domains displayed in Fig. 2.35(iii) and Fig. 2.35(a). Distances of 0.4300 nm between characteristic rows of bright lines are observed in Fig. 2.35(B). If this value is transformed into that of cubic double perovskite structure, a value of 0.8600 nm is obtained,
which is consistent with the lattice parameter obtained from neutron diffraction refinement. Lattice fringes in Fig. 2.35(A), indicating √2/2 value (0.3048 nm) of that in Fig. 2.35(B) periodicity along this direction, is a reflection of ordering in the A area. The EDS nano-analysis performed on the crystal areas in STEM mode did not show differences in the chemical composition between domains of the crystals as shown in Fig. 2.34(ii) and Fig. 2.35(ii), with more Y and less Nb concentrations in BCNY0.3 samples. It is noted that for fully ordered complex perovskites, such as fully B-site ordered {\text{D}t\text{Sr}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9.3}}^{39} and A site and B-site doubly ordered complex perovskite {\text{KLaMnWO}}_{6}^{40} they show clearly ordered and even chessboard patterned TEM images and superlattice reflections in SAED patterns. It is believed that the cation ordering of the structures will reasonably result in oxygen vacancy domains of ordered clusters, which nucleate at dopant ions with negative charges to form defect associates/complexes in the structure (such as the potential {\text{v}}_{\text{O}}^{\text{Y}}\text{Nb} defect complex in our material system).\textsuperscript{36} Therefore, a lower degree of cation ordering for the Y doped samples leads to oxygen vacancy disordering which should be beneficial for ionic transport in these material systems.

Table 2.7 Structural parameters for selected samples by neutron diffraction and Rietveld refinement.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>BCN18</th>
<th>BCNY0.2</th>
<th>BCNY0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>8.4077(5)</td>
<td>8.4368(6)</td>
<td>8.4473(5)</td>
</tr>
<tr>
<td>CaO wt%</td>
<td>0</td>
<td>0.325(42)</td>
<td>0.963(37)</td>
</tr>
<tr>
<td>Rwp</td>
<td>0.0466</td>
<td>0.0491</td>
<td>0.0524</td>
</tr>
<tr>
<td>Rp</td>
<td>0.0378</td>
<td>0.0361</td>
<td>0.0401</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>5.30</td>
<td>5.49</td>
<td>6.55</td>
</tr>
<tr>
<td>Ba 8c ((\frac{1}{4}, \frac{1}{4}, \frac{1}{4}))</td>
<td>Uiso (Å(^2))</td>
<td>0.01253(25)</td>
<td>0.01522(31)</td>
</tr>
<tr>
<td></td>
<td>Occup.</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Nb 4a (0, 0, 0)</td>
<td>Uiso (Å(^2))</td>
<td>0.00826(39)</td>
<td>0.01111(64)</td>
</tr>
<tr>
<td></td>
<td>Occup.</td>
<td>0.213</td>
<td>0.217(38)</td>
</tr>
<tr>
<td>Ca 4a (0, 0, 0) +</td>
<td>Uiso (Å(^2))</td>
<td>0.00826(39)</td>
<td>0.01111(64)</td>
</tr>
<tr>
<td></td>
<td>Occup.</td>
<td>0.787</td>
<td>0.757(2)</td>
</tr>
<tr>
<td>Y 4a (0, 0, 0)</td>
<td>Uiso (Å(^2))</td>
<td>-</td>
<td>0.01111(64)</td>
</tr>
<tr>
<td></td>
<td>Occup.</td>
<td>-</td>
<td>0.026(38)</td>
</tr>
<tr>
<td>Nb 4b ((\frac{1}{2}, \frac{1}{2}, \frac{1}{2}))</td>
<td>Uiso (Å(^2))</td>
<td>0.00433(30)</td>
<td>0.00376(42)</td>
</tr>
<tr>
<td></td>
<td>Occup.</td>
<td>1.00</td>
<td>0.889(38)</td>
</tr>
<tr>
<td>Y 4b ((\frac{1}{2}, \frac{1}{2}, \frac{1}{2}))</td>
<td>Uiso (Å(^2))</td>
<td>-</td>
<td>0.00376(42)</td>
</tr>
<tr>
<td></td>
<td>Occup.</td>
<td>-</td>
<td>0.111(38)</td>
</tr>
<tr>
<td>O 24e (x, 0, 0)</td>
<td>x</td>
<td>0.2625(1)</td>
<td>0.2646(1)</td>
</tr>
<tr>
<td></td>
<td>Uiso (Å(^2))</td>
<td>0.02340(31)</td>
<td>0.02280(37)</td>
</tr>
<tr>
<td></td>
<td>Occup.</td>
<td>0.940(2)</td>
<td>0.909(2)</td>
</tr>
<tr>
<td></td>
<td>Occup. (Cal.)</td>
<td>0.970</td>
<td>0.948</td>
</tr>
</tbody>
</table>

\(^+\): The Ca occupancy is calculated according to the weight fraction of CaO.
Figure 2.34 (i) SAED pattern of BCNY0.2 sintered powder along the [111] zone axis of the sample powder aligned parallel to the electron beam, (ii) EDS of the selected area (iii) HRTEM image corresponding to the [111] zone axis of the sample, and (A-C) magnifications of A, B, C domains, respectively, (a-c) Fast Fourier Transform (FFT) of the magnified domains, respectively.

Figure 2.35 (i) SAED pattern of BCNY0.3 sintered powder along the [100] zone axis of the sample powder aligned parallel to the electron beam, (ii) EDS of the selected area (iii) HRTEM image corresponding to the [100] zone axis of the sample, and (A-B) magnifications of A and B domains, (a-b) FFT of the magnified domains, respectively.

Table 2.8 Relative intensities of selected peaks which indicate the degree of cation ordering of the samples.

<table>
<thead>
<tr>
<th>Intensity ratio</th>
<th>(111)/(220)</th>
<th>(113)/(220)</th>
<th>(113)/(222)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCN18</td>
<td>0.02458</td>
<td>0.01315</td>
<td>0.09456</td>
</tr>
<tr>
<td>BCNY0.3</td>
<td>0.02293</td>
<td>0.00726</td>
<td>0.06066</td>
</tr>
<tr>
<td>BCNY0.5</td>
<td>0.01680</td>
<td>0.00489</td>
<td>0.04174</td>
</tr>
</tbody>
</table>

The activation energy values for the samples are 0.75±0.02, 0.55±0.01, 0.59±0.01, 0.54±0.01, and 0.52±0.01 eV, for BCN18, BCNY0.1, BCNY0.2, BCNY0.3, and BCNY0.5, respectively, showing a decrease with Y doping. As shown in the inset in Fig. 2.36, the
conductivity increases with Y concentration reaching 0.3 and then decreasing with x=0.5, with BCNY0.3 showing the highest conductivity of 5.3×10⁻³ S cm⁻¹ at 600°C in wet air, a value with 2.4 times improvement compared to undoped BCN18 (2.2×10⁻³ S cm⁻¹ at 600°C). This value is also comparable to the state-of-the-art Zr doped BaCeO₃ based materials. BCNY0.3 shows higher conductivity than BaZr₀.₃Ce₀.₅Y₀.₂O₃₋𝛿 while exhibits much better stability towards CO₂ and/or water. The activation energy of the total conductivity is influenced by the charge carriers existing in both bulk (grain) and grain boundary regions of the samples. For proton conductors, the main charge carriers are proton defects, which are formed mainly via equation (2.13). The protons (-OH group) are rotationally diffused, hopping between adjacent oxygen ions within the perovskite structure and leading to long range proton conduction without movement of oxygen ions. Besides proton defects, there are also other charge carriers such as electronic holes (h⁺) and electrons (e⁻). Under high oxygen partial pressure, p-type conduction represented in reactions (2.16) and (2.17) will be favored:

\[ V_o + \frac{1}{2}O_2 = O_2^+ + 2h \quad (2.16) \]
\[ 20H_2O + \frac{1}{2}O_2 = 20O_2^+ + H_2O + 2h \quad (2.17) \]

![Figure 2.36](image)

**Figure 2.36** Arrhenius plots of the total conductivity of the samples in humidified air. Inset is the conductivity as a function of yttrium concentration.

Consequently, increase in the oxygen partial pressure will result in consumption of oxygen vacancies and proton defects, leading to a decrease in proton conductivity and/or an increase in electronic conductivity. In the presence of very reducing atmospheres such as in dry hydrogen, hydrogen will react with oxide ions in the lattice producing hydroxide groups and electrons. In addition, under reducing environment, oxygen may leave the lattice creating oxygen vacancies and electrons.

The temperature also affects the movement of the defects. As it can be seen in Fig. 2.36, with the increase in testing temperature, the conductivity increases almost linearly in the Arrhenius plot due to the increased mobility of proton defects in a thermally activated process. At higher temperatures (> 600°C) the activation energy decreases slightly due to the occurrence of water desorption in the structure, resulting in a decrease in the proton concentration. The electronic hole and/or oxygen ionic conduction appears and are expected to dominate when temperature further increases.
Figure 2.37 Bulk conductivity for selected samples measured at different atmospheres.

The measured conductivity in Fig. 2.36 is the total conductivity of the materials, to which both bulk and grain boundary conduction contribute, while the bulk conductivity reflects the intrinsic properties of the materials. The bulk and grain boundary (GB) conductivity can be separated at lower temperature regime by fitting with RC equivalent circuit to the impedance spectra. Fig. 2.37 shows the bulk conductivity for selected samples in different atmospheres. Overall, it can be seen that BCNY0.3 shows the highest bulk conductivity in all atmospheres, followed by BCNY0.5, while BCN18 shows the lowest bulk conductivity. This can be explained in accordance with previous results that the introduction of up to 30% yttrium into BCN18 (BCNY0.3) has resulted in more oxygen vacancies into the system, while at the same time leading to less cation ordering of the structure and hence improved bulk proton conductivity. Further doping of Y for BCNY0.5 resulted in composition changes in the bulk (Ba evaporation), and the sample consequently showed lower bulk proton conductivity. The possible \( V_{0,\text{bcn0.5}} \) clustered defects due to the excessive amount of \( V_0 \) in the bulk may also affect the effective oxygen vacancy amount and cause lower bulk conductivity. The activation energy for the bulk conduction ranges from 0.52 to 0.59 eV, characteristic of proton conduction.

Figure 2.38 Bulk and grain boundary (GB) conductivity for BCNY0.3 at different atmospheres.
Fig. 2.38 shows the bulk and grain boundary (GB) conductivity for sample BCNY0.3 measured at low temperature regime (from 100-400ºC) in ambient air, wet air and wet H₂, respectively. From Fig. 2.38(a) it can be seen that the bulk conductivity changes as a function of oxygen partial pressure. The bulk conductivity in wet air and wet H₂ is higher than that in ambient air, which is indicative of proton conduction in the bulk area due to the introduction of water and hydrogen, respectively. Activation energy of 0.57 eV is also characteristic of proton conduction. For the grain boundary conductivity, the sample in wet H₂ shows a lower GB conductivity than in wet air and ambient air, indicating that protons are not the dominant charge carriers in the grain boundary area. Rather, p-type (electronic hole) conduction should appear at higher oxygen partial pressure based on the reactions (5) and (6). Higher activation energy in air than in H₂ (0.77 vs. 0.70 eV) for BCNY0.3 is also indicative of the enhancement of electronic hole conduction.

To investigate the chemical stability of the Y-doped BCN18 compounds, the sintered pellets were ground into powders and then exposed to boiling water for 24 h. The treated powders were then examined by XRD, as shown in Fig. 2.39. The XRD pattern of BaZr₀.₁Ce₀.₇Y₀.₁Yb₀.₁O₃₋δ (BZCYYb) powder treated in boiling water for 4 h was compared as a reference. As shown in Fig. 2.39, simple perovskite structure BaCeO₃ based proton conductors readily decompose in boiling water to form Ba(OH)₂ and CeO₂, or react with CO₂ in the air to form BaCO₃. BaCeO₃ decomposed into the prevalent CeO₂ and BaCO₃ impurity phase, while Ba(OH)₂ was dissolved in water. For complex perovskite structured BCN18 based proton conductors, they retained the perovskite structure without detectable impurities after exposure in boiling water for 24 h. It is clear that BCN18 based proton conductors are thermodynamically more stable than BZCYYb when treated in boiling water, and the introduction of yttrium did not show any detrimental effect on the chemical stability.

The stability of Y-doped BCN18 towards CO₂ atmosphere also showed little change in terms of crystal structure. The sintered pellets were exposed to air containing 3 vol% CO₂ and 3 vol% H₂O at 700ºC for 24 h. The XRD patterns of the surfaces of the pellets were collected after the treatments as shown in Fig. 2.39(b). No secondary phases can be observed for the differently treated BCN18 sintered pellets in all the XRD patterns, consistent with the reports for BCN18 based system.⁵, ⁴³ Stability tests on BaCe₀.₇Y₀.₃O₃₋δ and BaIn₀.₁Ce₀.₇Y₀.₂O₃₋δ samples were also included for comparison, both of which showed decomposition. The BCN18 based samples treated in pure CO₂ at 700ºC extreme conditions did not show any observable phase decomposition and secondary phase formation. Thermogravimetry results in CO₂ atmosphere also confirmed the chemical stability in CO₂ gases. Water and CO₂ stability test results suggest that the Y-doped BCN18 samples showed sufficient chemical stability even in harsh conditions and the stability is not affected by the yttrium doping concentration up to 0.3. It can be seen that BCNY0.3 shows very promising chemical stability among the reported intermediate temperature perovskite proton conductors and acceptable conductivity compared with the state-of-the-art Ba(Zr;Ce)O₃ based proton conductors.
In Summary, Novel complex perovskite structured $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82-x}\text{Y}_x\text{O}_{9-\delta}$ proton conducting materials have been synthesized and characterized. Neutron powder diffraction and HRTEM determined the crystal structure as well as the cation ordering of the materials. Partial substitution of $\text{Nb}$ by $\text{Y}$ effectively introduced more oxygen vacancies and reduced the degree of cation ordering, leading to increased ionic carrier concentration, mobility of the carriers, and consequently improved proton conductivity, specifically in the bulk areas. The optimum composition was determined to be $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.52}\text{Y}_{0.3}\text{O}_{9-\delta}$ which possessed the highest proton conductivity among all the different $\text{Y}$ doping concentrations and exhibited exceptional chemical stability towards water and $\text{CO}_2$.

2.4.7 First principles assessment of perovskite dopants for proton conductors with chemical stability and high proton conductivity

For proton conducting oxides, proton migration in doped perovskites occurs through two elementary steps: the transfer of protons between adjacent oxide ions and a rotation. Kreuer noted that proton diffusion can be affected by a reduction of symmetry and local structural and chemical perturbations by dopants.66 One potential problem with ceramic proton conductors with basic components such as $\text{Sr}$ and $\text{Ba}$ is that they are susceptible to carbonate formation in environments containing $\text{CO}_2$.67 In considering ceramics for proton-conducting applications, chemical stability and proton conductivity are both important. Cerates and zirconates both exhibit significant proton conductivity.68 Iwahara et al. found high proton conduction in $\text{SrCeO}_3$ and $\text{BaCeO}_3$.69,70 However, unlike cerates, which have poor stability with respect to carbonate formation, zirconates are proton conductors with good chemical stability.71 Acceptor-doped $\text{BaZrO}_3$, in which $\text{Zr}^{4+}$ is substituted with a trivalent dopant, has attracted considerable attention as an example of a material with these properties. Y-doped $\text{BaZrO}_3$ is one such promising material providing excellent chemical stability and high protonic conductivity.72 There are a large number of possible trivalent dopants that can be used in $\text{BaZrO}_3$. Therefore, it is interesting to ask how the stability with respect to carbonate formation and the overall proton conductivity vary among these dopants. In this paper, we examine this question using first-principles density functional theory (DFT) calculations. In this paper, we use efficient methods to examine a wide
range of possible dopants: Y, In, Ga, Sc, Nd, Al, Tl, Sm, Dy, La, Pm, Er, and Ho. Our results are based on DFT calculations of the reaction free energies at finite temperatures, which allow us to predict the phase stability of oxide and carbonate phases as functions of temperature and CO₂ pressure. We then consider the mobility of protons in each material. Proton diffusion is described by using extensive DFT calculations to determine the activation energies and hopping prefactors for local hops by protons and then incorporating this information within a lattice model for the doped material to determine net proton mobilities. Our calculations identify a small number of dopants that are known from prior experiments and simulations to have enhanced diffusivity relative to pure BaZrO₃ and also identify several new dopants with this property. Because of the large number of dopants included in our calculations, our results create a useful opportunity to explore the physical origins of the trends in chemical stability and proton mobility among different dopants. We explore several possible physical descriptors that can be used for this purpose.

Table 2.9 A comparison of the experimental and the DFT calculated structural parameters for the 17 crystalline compounds considered in our calculations, with all lengths in Å and angles in degrees.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Structural parameters (Å, degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>P12_1/c1</td>
<td>a = 5.143, b = 5.204, c = 5.310, β = 99.166</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Pm-3m</td>
<td>a = 5.414, b = 5.446, c = 5.546</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>Ia-3</td>
<td>a = 10.611, a = 10.694, a = 10.694</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>R-3cH</td>
<td>a = 4.983, c = 13.433, γ = 120</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>Ia-3</td>
<td>a = 10.117, a = 10.334, a = 10.334</td>
</tr>
<tr>
<td>Sc₂O₃</td>
<td>Ia-3</td>
<td>a = 9.849, a = 9.901, a = 9.901</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>P-3mI</td>
<td>a = 3.827, c = 6.070</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>R-3cH</td>
<td>a = 4.762, c = 12.999, γ = 120</td>
</tr>
<tr>
<td>Tl₂O₃</td>
<td>Ia-3</td>
<td>a = 10.543, a = 10.890, a = 10.890</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>P-3mI</td>
<td>a = 3.940, a = 3.939, c = 6.130, γ = 120</td>
</tr>
<tr>
<td>Pm₂O₃</td>
<td>Ia-3</td>
<td>a = 11.065, a = 11.065, a = 11.065</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>Ia-3</td>
<td>a = 10.920, a = 10.990, a = 10.990</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>Ia-3</td>
<td>a = 10.67, a = 10.660, a = 10.660</td>
</tr>
<tr>
<td>Ho₂O₃</td>
<td>Ia-3</td>
<td>a = 10.606, a = 10.606, a = 10.606</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>Ia-3</td>
<td>a = 10.548, a = 10.533, a = 10.533</td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>Pm-3m</td>
<td>a = 4.188, a = 4.252</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>Pnma</td>
<td>a = 6.334, b = 5.315, c = 8.904</td>
</tr>
</tbody>
</table>

The optimized lattice constants for each compound considered in this work are presented in Table 2.9 along with the corresponding experimental data. Predicted values agree to within
3% of experimental lattice constants and angles, indicating a good agreement. Calculated lattice constants using the GGA functional were slightly larger than the experimental lattice constants apart from La$_2$O$_3$, Pm$_2$O$_3$, Dy$_2$O$_3$, Ho$_2$O$_3$ and Er$_2$O$_3$.

The carbonate formation reactions of doped BaZrO$_3$ in the presence of CO$_2$ can be expressed as

$$\text{BaZr}_{0.75}\text{M}_{0.25}\text{O}_{3-\delta} + \text{CO}_2 = \text{BaCO}_3 + 0.75\text{ZrO}_2 + 0.25\text{M}_2\text{O}_3$$

(2.18)

where M is a trivalent dopant such as Y, In, Ga, Sc, Nd, Al, Tl, Sm, Dy, La, Pm, Er or Ho. We initially performed our calculations with the dopant-free system and found that at 323 K the free energy for the reaction (2.8) was -70.8 kJ mol$^{-1}$. The experimental result at the same temperature is 283.6 kJ mol$^{-1}$. This level of agreement between DFT-calculated and experimental free energies is similar to what has been observed for a variety of metal hydride decomposition reactions.

After we investigated the stability of BaZrO$_3$, we extended our calculations to materials doped with M$^{3+}$ at the Zr site. Initially we examined the chemical stability of the common dopants, Y, In, Ga and Sc in BaZrO$_3$. When the dopants are present, oxygen vacancies are created to maintain overall charge neutrality. Our calculations used a dopant concentration of 2/8 (25%), so the net stoichiometry of the doped materials was Ba$_8$Zr$_6$Y$_2$O$_{23}$. Our calculations for doped BaZrO$_3$ used 2 $\times$ 2 $\times$ 2 unit cells in the computational supercell, so each supercell contained two dopant atoms and one O vacancy. After creating the O vacancy in the supercell, calculations were performed with various dopant atom configurations. The arrangement with the lowest energy was used for the calculation of the VDOS. For Y, In, Ga, Sc, Al, Tl, Dy, Er and Ho, this state had two dopant atoms placed next to each other, whereas the two dopants in the lowest energy state for Nd, Sm, La and Pm were separated by 7.62, 7.60, 7.65 and 7.60 Å, respectively.

The equilibrium CO$_2$ pressure associated with carbonate formation of undoped BaZrO$_3$ as predicted by our calculations is shown in Fig. 2.40, using $P_0 = 1$ bar. We denote the temperature at which carbonate formation becomes favorable as $T^\ast$. As the CO$_2$ pressure increases, the critical temperature increases. For CO$_2$ pressures of 0.01, 0.1, 1.0 and 10.0 bar, $T^\ast$ of the undoped material is calculated to be 576, 627, 688 and 763 K, respectively. Among the set of materials, perovskites with higher critical temperatures are more susceptible to carbonate formation and are less chemically stable. As every material we considered depends on CO$_2$ pressure in the same way, we only report results with a CO$_2$ pressure of 1 bar below.
A stability diagram for the doped materials investigated is shown in Fig. 2.41 for a CO₂ pressure of 1 bar. Fig. 2.41 shows that the rank of the chemical stability of MBaZrO₃ with respect to CO₂ is M = Ga (T* = 786 K), Sc (T* = 805 K), In (T* = 821 K), Y (T* = 875 K). Although yttrium is known to be a useful dopant to improve proton conductivity, it is not favorable in terms of the chemical stability compared to the other dopants we examined. This is consistent with an experimental study that found increasing the amount of Y dopant in BaIn₀.₃₋ₓYₓCe₀.₇O₃₋δ lowered the CO₂ tolerance.⁷⁸ For undoped BaZrO₃, the calculated value of T* is 688 K when P_CO₂ is 1 bar; each of the doped materials we studied showed a higher critical temperature than the undoped material.

Computing the VDOS of a solid is much more time consuming than a DFT total energy calculation. In the calculations above, each doped material requires 117 displacement calculations due to the broken symmetry associated with the dopants and oxygen vacancies, whereas the undoped material only needs 4 displacement calculations. Because of the computational expense of these calculations, it would be useful to have a simplified model to efficiently screen materials. This concept has proved to be useful, for example, in extensive computational studies of light metal hydrides for hydrogen storage.⁷⁹,⁸₀ We have developed a similar approach, noting that the VDOS were very similar for the materials described above with the same stoichiometries. Since calculating the thermodynamic properties involves the integration of the VDOS,⁸¹ the contributions of these vibrational effects to doped BaZrO₃ materials are quite similar. Fig. 2.42 shows that the temperature-dependent vibrational free energies of the solids are comparable for Y, In, Ga and Sc doped BaZrO₃. This implies that a far simpler calculation can be performed using DFT total energies and the finite temperature thermodynamics reliably estimated using a correction factor based on the detailed calculations in Fig. 2.42. Specifically, we define the correction factor as the average of the ΔF_solids for the four doped materials shown in Fig. 2.42.
Figure 2.41 Free energy of reaction, $\Delta G$, as a function of temperature for carbonate formation reactions. The undoped material is shown using unfilled squares for the reaction $\text{BaZrO}_3 + \text{CO}_2 = \text{BaCO}_3 + \text{ZrO}_2$. The results for the doped materials correspond to the reaction $\text{Ba}_8\text{Zr}_6\text{M}_2\text{O}_{23} + 8\text{CO}_2 = 8\text{BaCO}_3 + 6\text{ZrO}_2 + \text{M}_2\text{O}_3$ for $\text{M} = \text{Y, In, Ga and Sc}$.

Figure 2.42 $\Delta F_{\text{solids}}$ as a function of temperature for the carbonate formation reaction of $\text{BaZrMO}_{3-\delta}$, where $\text{M} = \text{Y, In, Ga, Sc}$, with energy in eV and temperature in K.
To test the predictive power of this simplified approach, we performed calculations for two additional dopants, Al and Nd, in BaZrO$_3$. For each dopant, we calculated the reaction free energy using the DFT-calculated VDOS as described above. We also estimated the reaction free energy from the sum of their DFT total energies and the correction factor defined above. The agreement between these two kinds of calculations is shown in Fig. 2.43. The simplified calculation predicted $T^*$ for Al doped BaZrO$_3$ to be 832 K and 914 K for Nd doped BaZrO$_3$, while the detailed calculations give the $T^*$ for Al doped BaZrO$_3$ as 830 K and 920 K for Nd doped BaZrO$_3$. These results indicate that the simplified method introduced above can accurately predict the stability of doped BaZrO$_3$ materials.

Now that the simplified model has been validated, we can rapidly examine a large number of potential dopants using DFT total energy calculations at 0 K with the correction factor to predict the temperature dependent free energy. Data from this approach is shown in Table 2.10. From these results, we can rank the CO$_2$-stability of the trivalent dopants in BaZrO$_3$. Among the other rare earth dopants, Dy, Er and Ho showed better chemical stability with respect to CO$_2$ compared with Y.

In our DFT calculations, one Zr$^{4+}$ ion in a simulation volume of a $2 \times 2 \times 2$ unit cell was replaced by a trivalent dopant M$^{3+}$. The dopant concentration in our system was therefore 1/8 (12.5%), which is comparable to the dopant concentration (10%) in the experiments discussed by Kreuer et al. The doped simulation box becomes charge neutral after a proton is introduced. Within this volume, we identified seven representative environments that define different energy barriers for proton transfer and three representative environments that define different energy barriers for proton rotation. These hops are listed in Table 2.11. This classification assumes that the environments associated with each hop can be defined using only the nearest neighbors of the proton in its initial and final site. More involved methods exist to relax this assumption and develop more precise models for specific materials of interest.

![Fig. 2.43](image) The absolute difference in the free energy between the simplified and detailed models of Al and Nd doped BaZrO$_3$.  

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Table 2.10 The predicted critical temperature of Ba₈Zr₆M₂O₂₃ from the simplified model described in the text, with dopants ordered by increasing T*.

<table>
<thead>
<tr>
<th>Dopant (M)</th>
<th>T* (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>789</td>
</tr>
<tr>
<td>Sc</td>
<td>799</td>
</tr>
<tr>
<td>In</td>
<td>826</td>
</tr>
<tr>
<td>Al</td>
<td>832</td>
</tr>
<tr>
<td>Er</td>
<td>857</td>
</tr>
<tr>
<td>Ho</td>
<td>863</td>
</tr>
<tr>
<td>Tl</td>
<td>867</td>
</tr>
<tr>
<td>Dy</td>
<td>870</td>
</tr>
<tr>
<td>Y</td>
<td>872</td>
</tr>
<tr>
<td>Sm</td>
<td>903</td>
</tr>
<tr>
<td>Pm</td>
<td>911</td>
</tr>
<tr>
<td>Nd</td>
<td>914</td>
</tr>
<tr>
<td>La</td>
<td>932</td>
</tr>
</tbody>
</table>

Table 2.11 A summary of the distinct transition states where a dopant is the nearest neighbor of the initial or final proton, where M = Ga, Sc, In, Al, Er, Ho, Tl, Dy, Y, Sm, Pm, Nd and La.

<table>
<thead>
<tr>
<th>Nearest neighbor to the initial proton</th>
<th>Nearest neighbor to the final proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transfer 1</td>
<td>M, M</td>
</tr>
<tr>
<td>Transfer 2</td>
<td>M, Zr</td>
</tr>
<tr>
<td>Transfer 3</td>
<td>Zr, M</td>
</tr>
<tr>
<td>Transfer 4</td>
<td>M, M</td>
</tr>
<tr>
<td>Transfer 5</td>
<td>Zr, Zr</td>
</tr>
<tr>
<td>Transfer 6</td>
<td>Zr, Zr</td>
</tr>
<tr>
<td>Transfer 7</td>
<td>Zr, Zr</td>
</tr>
<tr>
<td>Rotation 1</td>
<td>M, M</td>
</tr>
<tr>
<td>Rotation 2</td>
<td>Zr, M</td>
</tr>
<tr>
<td>Rotation 3</td>
<td>Zr, Zr</td>
</tr>
</tbody>
</table>

We determined the energy barriers for the 10 proton hops using DFT calculations for each of the 13 dopants in BaZrO₃. These energy barriers are listed in the ESI. At each transition state, there are two real frequencies and one imaginary frequency when it is assumed that all atoms are fixed except the proton.

Once the proton hopping rates were defined, we performed KMC simulations to obtain the diffusivity of the proton in doped BaZrO₃. In our KMC simulations, we defined a simulation volume consisting of randomly arranged atoms of the oxide at the desired composition of a trivalent dopant. The simulation volume size included 5×5×5 unit cells. The hopping dynamics of the protons were then simulated using a simple algorithm that correctly reproduces the local hopping rates. At each time step a proton is randomly selected from all the protons in the simulation volume and a move direction is chosen randomly from the two possible directions available for a transfer and the two possible directions available for a rotation. Hops are accepted with a probability defined by the ratio of the attempted rate and the maximum rate possible in the simulation volume. Time is incremented by \((4k_{fast}N_{H^+})^{-1}\) regardless of the success of the attempted hop, where \(N_{H^+}\) is the number of protons in the simulation volume and \(k_{fast}\) is the fastest hopping rate of all possible hops in the volume. The overall proton self-diffusivity was determined using an Einstein expression relating the diffusivity to the mean square displacement. The mean squared displacement increases linearly, with time and a diffusion coefficient can be obtained from the slope.

The effective activation energy for proton diffusion in each doped material is listed in
Table 2.12. We found that a number of the dopants, including La, Pm, Nd and Tl, have lower effective diffusion energy barriers than Y. Islam et al. pointed out that smaller dopants form stronger hydrogen bonds so that the hydroxyl-dopant association makes the diffusion of a proton more difficult. This trend is followed qualitatively by our results, where dopants with larger ionic radii tend to have smaller effective diffusion activation energies.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$E_d$ (eV)</th>
<th>Effective ionic radius$^{50}$ (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.583</td>
<td>53.5</td>
</tr>
<tr>
<td>Ga</td>
<td>0.522</td>
<td>62</td>
</tr>
<tr>
<td>Sc</td>
<td>0.588</td>
<td>74.5</td>
</tr>
<tr>
<td>In</td>
<td>0.439</td>
<td>80</td>
</tr>
<tr>
<td>Tl</td>
<td>0.276</td>
<td>88.5</td>
</tr>
<tr>
<td>Er</td>
<td>0.325</td>
<td>89</td>
</tr>
<tr>
<td>Y</td>
<td>0.285</td>
<td>90</td>
</tr>
<tr>
<td>Ho</td>
<td>0.33</td>
<td>90.1</td>
</tr>
<tr>
<td>Dy</td>
<td>0.302</td>
<td>91.2</td>
</tr>
<tr>
<td>Sm</td>
<td>0.29</td>
<td>95.8</td>
</tr>
<tr>
<td>Pm</td>
<td>0.264</td>
<td>97</td>
</tr>
<tr>
<td>Nd</td>
<td>0.282</td>
<td>98.3</td>
</tr>
<tr>
<td>La</td>
<td>0.283</td>
<td>103.2</td>
</tr>
</tbody>
</table>

Our results for the full set of doped materials we considered are summarized in Table 2.13. A striking observation from Table 2.13 is that the relative proton conductivities among the doped materials vary by several orders of magnitude relative to the Y-doped material at 600 K. The variation in $s_1/s_2$ diminishes at higher temperatures. For example, at 1000 K, $s_1/s_2$ is 0.003 for La and 1155 for Sc.

Our results in Tables 2.10 and Table 2.13 rank the chemical stabilities of the doped materials as Ga > Sc > In > Al > Er > Ho > Tl > Dy > Y > Sm > Pm > Nd > La while the rank for proton conductivity at 600 K is La > Nd > Pm > Sm > Tl > Dy > Ho > Er > Al > In > Ga > Sc, respectively. The ranking changes slightly at higher temperatures due to variations in the diffusion prefactors, but these changes are minor. Since the ratio of the diffusion prefactors varies only moderately, we focus on the diffusion energy barrier and relative formation energy to characterize the contributions of mobility and concentration to the overall conductivity.

It is useful to explore the physical origin of the trends seen in our calculations. Previously, Kreuer et al. proposed that the ionic radius of a dopant, the electronegativities of the cations and the corresponding acid/base properties of the oxide ions are important for the mobility of protons in perovskites. To examine the physical background behind the net energy barrier for proton conductivity and the critical temperature for carbonate formation, we investigated the relationships between these properties and the Pauling electronegativity of the dopant and the ionic radius of the dopant. These relationships are shown in Fig. 2.44 and 2.45, respectively.
Table 2.13 A summary of the proton conductivity of M-doped materials relative to Y-doped BaZrO$_3$ ($s_1/s_2$) at T = 600 K. All energies are shown in eV.

<table>
<thead>
<tr>
<th>M</th>
<th>$\Delta E_f$</th>
<th>$\Delta E_d$</th>
<th>$A_1/A_2$</th>
<th>$\sigma_1/\sigma_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.487</td>
<td>0.002</td>
<td>0.956</td>
<td>7.5 x 10^{-5}</td>
</tr>
<tr>
<td>Nd</td>
<td>0.320</td>
<td>0.002</td>
<td>0.970</td>
<td>0.002</td>
</tr>
<tr>
<td>Pm</td>
<td>0.255</td>
<td>0.021</td>
<td>1.225</td>
<td>0.006</td>
</tr>
<tr>
<td>Sm</td>
<td>0.206</td>
<td>-0.005</td>
<td>0.862</td>
<td>0.017</td>
</tr>
<tr>
<td>Tl</td>
<td>0.087</td>
<td>0.008</td>
<td>1.290</td>
<td>0.202</td>
</tr>
<tr>
<td>Dy</td>
<td>0.008</td>
<td>-0.017</td>
<td>0.900</td>
<td>1.072</td>
</tr>
<tr>
<td>Ho</td>
<td>-0.033</td>
<td>-0.046</td>
<td>0.544</td>
<td>2.496</td>
</tr>
<tr>
<td>Er</td>
<td>-0.076</td>
<td>-0.040</td>
<td>0.676</td>
<td>6.376</td>
</tr>
<tr>
<td>Al</td>
<td>0.209</td>
<td>-0.299</td>
<td>1.740</td>
<td>9.823</td>
</tr>
<tr>
<td>In</td>
<td>-0.315</td>
<td>-0.154</td>
<td>0.245</td>
<td>2134</td>
</tr>
<tr>
<td>Ga</td>
<td>-0.220</td>
<td>-0.237</td>
<td>2.015</td>
<td>13 816</td>
</tr>
<tr>
<td>Sc</td>
<td>-0.405</td>
<td>-0.303</td>
<td>0.314</td>
<td>275 420</td>
</tr>
</tbody>
</table>

Laidoudi et al. found that proton conductivity decreases in Er, Ho, Tm, Yb and Y doped materials as the electronegativity increases up to the electronegativity of 1.4. The decrease of the difference in electronegativity between A- and B-site cations in ABO$_3$-type perovskites increases the proton concentration since the hydration enthalpy becomes more negative. Ba (the A site cation) has a Pauling electronegativity of 0.89, and Zr (the B site cation) has a Pauling electronegativity of 1.33. This suggests that dopants that are closer in electronegativity to Ba will have better proton conductivity due to increased proton concentration. The results in Fig. 2.44 agree with this description since $\Delta E_f + \Delta E_d$ decreases as the dopant electronegativity increases for dopants less electronegative than Zr. Four of the five dopants with the highest proton conductivities, Sm, Nd, La, and Pm, fall into this category.

Kreuer et al. found that higher dopant electronegativity leads to the high stability. Liu et al. found that there was no carbonate formation reaction in their XRD studies after they introduced 10% of Nb in BaCe$_{0.8}$Sm$_{0.2}$O$_{3-x}$. They concluded that the higher electronegativity of Nb decreases the basicity of BaCe$_{0.8}$Sm$_{0.2}$O$_{3-x}$ and restrains the reaction with CO$_2$. In other words, after the system has the adequate acidity, it enhances the chemical stability with respect to the carbonate formation reaction. This trend can also be seen in our results for dopants with electronegativities less than Ba in Fig. 2.44. Thus, the materials with a smaller electronegativity than Ba show a relatively simple relationship between electronegativity and both proton conductivity and chemical stability. The results in Fig. 2.44, however, show that no such simple relationship exists for dopants whose electronegativities are higher than Ba.
Figure 2.44 The relationships between $\Delta E_f + \Delta E_d$ (eV), critical temperature, and the Pauling electronegativity of the dopants we studied.

The critical temperature for carbonate formation and the net energy associated with proton mobility, $\Delta E_f + \Delta E_d$, is shown as a function of the dopant ionic radius in Fig. 2.45. Apart from Al- and Ga-doped materials, both quantities increase as the ionic radius of the dopant increases. This means proton conductivity increases as ionic radius increases but this also results in reduced chemical stability. This observation is consistent with previous experimental observations. Islam et al. found that larger dopants showed a weaker binding energy for hydroxyl–dopant pairs. Specifically, they found a stronger dopant–OH association in Sc-doped BaZrO$_3$ (the small ionic radius dopant case) than in In or Y doped BaZrO$_3$ (the large ionic radius dopant case). Matsumoto et al. examined the chemical stability of BaCeO$_3$ with various trivalent dopants with thermogravimetry (TG) and found that the critical temperature decreases with decreasing ionic size of the dopants and emphasized that chemical stability is affected by the size of the dopants. A central goal of our calculations was to examine whether there are dopants for BaZrO$_3$ that would enhance both its chemical stability and proton conductivity. This issue can be examined using Fig. 2.46, which plots $\Delta E_f + \Delta E_d$ as a function of $T^*$ for the complete set of materials we examined. For almost all of the materials, a simple trade-off is evident in which improvements in chemical stability (lower $T^*$) correspond to lower proton conductivity as characterized by $\Delta E_f + \Delta E_d$. The only exceptions to this trend are Ga- or Al-doped BaZrO$_3$. The existence of the simple trade-off depicted in Fig. 2.46 indicates that the choice of dopant for a particular application should be dictated by the relative importance given to chemical stability and proton conductivity.
2.4.8 Hydrogen permeation measurement

Dual phase ceramic (SrCeYbO$_{3-\delta}$) and metallic (Pd, Rh) membranes were fabricated in order to enhance the electronic conductivity and improve membrane separation efficiency. Metallic elements were chosen that would not oxidize under ceramic sintering conditions (1500 °C air) and were added in a “percolating” ratio of 40 volume % metal in 60 volume % ceramic to ensure a network of metallic conduction through the membrane thickness. X-ray diffraction analysis indicated no secondary phases were formed concomitant with metal additions. Permeation testing has been initiated on SrCeYbO$_{3-\delta}$ and dual phase materials using a gas feed of 1% H$_2$ with balance He in order to simulate the hydrogen isotope contamination levels expected.
in NGNP He cooled gas streams. The permeate side of the membrane was swept with argon gas and sent to a gas chromatograph to measure H₂ concentration in the gas stream along with any He that might have leaked through the membrane (pores) or sealing area from the feed stream. However, it was found that the 1% H₂ feed does not provide a large “driving force” for permeation and the Hydrogen detected in the GC had significant levels of Helium indicating leakage from ceramic or seal.

![Graph](image)

**Figure 2.47** Hydrogen permeation behavior of a 0.9-mm thick Ni-BZCYYb membrane at 900 °C when CO₂ was introduced and removed from the feed gas. Feed gas: 20 mL/min H₂, 47/50 mL/min He (dry or wet condition, respectively), 30 mL/min N₂/CO₂. Sweep gas: 20 mL/min N₂.

Although acceptor-doped BaCeO₃ and SrCeYbO₃₋δ shows the highest level of proton conductivities, they suffer from poor chemical stability in H₂O and CO₂. For example, hydrogen permeation flux of Ni–BaCe₀.₈Y₀.₂O₃₋δ diminished to zero in 30% CO₂ at 900 °C in ~20 h due to the formation of barium carbonate₁. The chemical stability of BaCeO₃ can be improved by doping Zr at the Ce sites, but with the expense of sharp reduction in proton conductivity and sintering activity. Ni–BaZr₀.₈ₓCe₀.₂O₃₋δ (0.4 ≤ x ≤ 0.7) membranes showed better chemical stability in CO₂ than Ni–BaCe₀.₈Y₀.₂O₃₋δ but still suffered serious performance losses during operation. The degradation was attributed to the insulating effect of BaCO₃ formed in the reaction between the membrane and CO₂. Recently, Yang et al. have reported that BaZr₀.₁Ce₀.₇Y₀.₁Yb₀.₁O₃₋δ (BZCYYb) possesses high proton conductivity and high tolerance to CO₂ and H₂S, showing excellent performance as anode materials in solid oxide fuel cells. Therefore, BZCYYb can potentially be a very promising material for hydrogen permeation membrane. Ni-BZCYYb cermet membrane was fabricated and its permeation behavior in CO₂ containing feed gas was investigated. Surprisingly, in many cases, the hydrogen permeation fluxes increased rather than decreased when CO₂ was introduced to feed gas, which cannot be explained by the generally-accepted perovskite and CO₂ reaction mechanism. This singular behavior inspires a detailed investigation on the mechanism, which can provide guidance on the development of CO₂-resistant hydrogen permeation membrane.

BZCYYb powder was synthesized by sol-gel combustion method and calcined at 1100 °C for 5h. Ni powder and BZCYYb powder were mixed in volume ratio of 40:60. The mixed
powder was uniaxially pressed and sintered at 1440 °C for 10 h in 4% H₂/N₂ to obtain Ni-BZCYYb membrane. The membrane was tested in a customer-built set-up for hydrogen permeability measurements. Fig. 2.47 shows the hydrogen permeation behavior of Ni-BZCYY membrane with and without CO₂ in the feed gas stream. In dry feed gas, when N₂ was replaced by CO₂, the hydrogen permeation fluxes increased by 2 times. In wet feed gas, the hydrogen permeation flux was also improved, but in less magnitude compared with that in dry hydrogen stream. Analysis of the exhaust feed gas showed considerable amount of CO and H₂O formation after CO₂ was introduced, accompanied by the decrease of H₂ concentration. The improvement of hydrogen permeation fluxes was ascribed to the increase of moisture content in feed gas, which acutely enhanced the proton conductivity of BZCYYb and hydrogen permeation flux of the membrane, especially in dry feed gas.
3. CONCLUSIONS

Both first principle calculations and the experimental preparations and characterizations have been explored to study the hydrogen isotope sequestration materials. As to the metal hydride materials, we have presented an investigation into the predicted thermodynamic stabilities of five metal hydrides ZrH₂, HfH₂, TiH₂, LiH, and NaH using four different levels of theory. The absorption of hydrogen and deuterium on a selected pure zirconium sample at elevated temperatures has been determined by experimental data. On the other hand, as to the development of high temperature proton conducting oxide materials, we have developed several novel high temperature proton conducting metal oxide ceramics with better stability and improved proton conductivity, including BaCe₀.₇In₀.₂Yb₀.₁O₃₋δ, doped Ba₃Ca₁.₈₂Nb₁.₈₂O₉₋δ, as well as microstructure modification of BaZr₀.₁Ce₀.₇Y₀.₁Yb₀.₁O₃₋δ and Ba₃Ca₁.₁₄Nb₁.₈₂O₉₋δ based proton conducting ceramics. First principle calculations of perovskite dopants for proton conductors with chemical stability and high proton conductivity have been demonstrated. The proton transfer and rotation mechanism in defect free KTO has been initially studied. Further first-principles calculations was addressed to the doped BaZrO₃ with efficient methods to examine a wide range of possible dopants (Y, In, Ga, Sc, Nd, Al, Tl, Sm, Dy, La, Pm, Er, and Ho). The physical origins of the trends in chemical stability and proton mobility among the different dopants have been investigated. Hydrogen permeation measurements have been done in dual Pd/Rh-SrCeYbO₃₋δ dual phase membranes, as well as the Ni-BaZr₀.₁Ce₀.₇Y₀.₁Yb₀.₁O₃₋δ (BZCYYb) hydrogen permeation membrane. Improvement of hydrogen permeation fluxes was found for Ni-BaZr₀.₁Ce₀.₇Y₀.₁Yb₀.₁O₃₋δ hydrogen permeation membrane, which was ascribed to the increase of moisture content in feed gas to acutely enhance the proton conductivity of BZCYYb and hydrogen permeation flux of the membrane, especially in dry feed gas. Significant progresses and extensive knowledge have been achieved in this project. However, further exploration on novel metal hydrides as well as novel high temperature proton conducting ceramics are still needed for effective tritium sequestration in high temperature nuclear energy systems.
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Journal Publications

3. Shumin Fang, Kyle Brinkman, Fanglin Chen, Hydrogen permeability and chemical stability of Ni-BaZr0.1Ce0.7Y0.1Yb0.1O3-δ membrane in concentrated H2O and CO2, Journal of Membrane Science, 467, 85-92 (2014).
7. Shumin Fang, Kyle Brinkman, Fanglin Chen, Unprecedented CO2-promoted hydrogen permeation in Ni-BaZr0.1Ce0.7Y0.1Yb0.1O3-δ membrane, ACS Applied Materials & Interfaces 6, 725-730 (2014)
10. Yao Wang, Han Wang, Tong Liu, Fanglin Chen, Changrong Xia, Improving the chemical stability of BaCe0.8Sm0.2O3-δ electrolyte by Cl doping for proton-conducting solid oxide fuel cell, Electrochemistry Communication 28, 87-90 (2013).
15. Fei Zhao, Siwei Wang, Latoya Dixon, Fanglin Chen, "Novel BaCe$_{0.7}$In$_{0.2}$Yb$_{0.1}$O$_{3-\delta}$ proton conductor as electrolyte for intermediate temperature solid oxide fuel cells", *Journal of Power Sources*, 196, 7500-7504 (2011).
16. Fei Zhao, Siwei Wang, Latoya Dixon, Fanglin Chen, "Novel BaCe$_{0.7}$In$_{0.2}$Yb$_{0.1}$O$_{3-\delta}$ proton conductor as electrolyte for intermediate temperature solid oxide fuel cells", *Fuel Cells Bulletin*, Volume 2011, Issue 9, September 2011, Pages 12-16.
17. Siwei Wang, Fei Zhao, Lingling Zhang, Kyle Brinkman, Fanglin Chen, Doping effect on complex perovskite structured Ba$_3$Ca$_{1.18}$Nb$_{1.82}$O$_9$-$\delta$ intermediate temperature proton conductor, *Journal of Power Sources*, 196, 7917-7923 (2011).

**Conference Presentations**
5. Siwei Wang, Min Tang, Kyle Brinkman, Fanglin Chen, Ion-irradiation-induced Reduction in Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6-\delta}$ Perovskite, *The 17th International Conference on Radiation Effects in Insulators (REI-2013)*, July 2013.
6. Shumin Fang, Kyle Brinkman, Fanglin Chen, Ni-BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ high flux CO$_2$-tolerant hydrogen permeation membrane, 223rd *Electrochemical Society Meeting*, Toronto, Canada, May 2013.


REFERENCES

50 J. Lv, L. Wang, D. Lei, H. Guo, R.V. Kumar, *J. Alloys Compd.*, 2009, 467, 376.
73 M. A. Gomez, M. Chunduru, L. Chigweshe, L. Foster, S.J. Fensin, K. M. Fletcher, L. E.