Characterizing Chemical Stability and Proton Conductivity of B-site Doped Barium Hafnate (BaHfO₃) and Barium Stannate (BaSnO₃) with First Principles Modeling

Sung Gu Kang^{a, b, *} and David S. Sholl^b

^a *School of Chemical Engineering, University of Ulsan, 93, Daehak-ro, Nam-gu, Ulsan 44610, Republic of Korea*

^b *School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Dr., Atlanta, GA 30332-0100, USA*

E-mail: sgkang@ulsan.ac.kr

Abstract

Perovskite-structured oxides are promising materials for proton conduction. We use first-principles calculations to investigate the chemical stability and proton conductivity of doped barium hafnate (BaHfO₃) and barium stannate (BaSnO₃). Previously, we [RSC Adv. **3**, 3333 (2013)] reported first-principles calculations examining the chemical stability and proton conductivity of B-site doped BaZrO₃ and found that Ga-doping gives the highest chemical stability and La-doping provides the highest proton conductivity in BaZrO₃. We use density functional theory (DFT) calculations to examine two other host materials, BaHfO₃ and BaSnO₃, using these two dopants, Ga and La. We find that doped BaHfO₃ is promising to study further in co-doping case, because Ga-doped BaHfO₃ demonstrates the high stability and La-doped BaHfO₃ shows the high proton conductivity compared to doped BaSnO₃ and doped BaZrO₃.

Keywords: perovskites, doping, DFT calculations, carbonates, proton conduction

1. Introduction

Ceramic materials are important for applications as sensors, thermoelectric devices and electrolytes in Solid Oxide Fuel Cells (SOFC) and high temperature proton conductors (HTPCs) for tritium separation [1-7]. Solid oxide proton-conducting electrolytes have been considered for SOFCs. These electrolytes can decrease the operation temperature to 500-700 °C from 800-1000 °C, the temperature required for oxygen ion conductors [1-4]. In the tritium separation application, sequestration of trace levels of tritium from Next Generation Nuclear Plant (NGNP) cooling systems is a significant challenge, since tritium is a radioactive fission product [5]. One potential way for separating tritium from exhaust gas streams is to use a proton conductor as a membrane [8].

Barium stannate (BaSnO_3) has a cubic structure and it is stable up to 1273 K [9]. BaSnO_3 has been used as a proton conductor [10-12]. Proton conductivity in Y-doped BaSnO_3 and In-doped BaSnO_3 has been studied [11, 12]. Experimentally, the proton conductivity in $\text{Ba}_2\text{YSnO}_{5.5}$ is $\sim 10^{0.2}$ K/ Ωcm at 1000 K [11], and the proton conductivity in $\text{BaIn}_{0.5}\text{Sn}_{0.5}\text{O}_{2.75}$ at 667 K with a proton content of 4.31 % is $\sim 10^{-0.5}$ K/ Ωcm [12]. In-doped BaSnO_3 shows high solubility of water for high temperature proton conductors, although it is unstable in hydrogen-rich atmospheres [12]. The proton migration energy barrier in In-doped BaSnO_3 was found to be 0.56 ± 0.03 eV [12]. Bévillon *et al.* examined hydration properties of La-doped BaSnO_3 using DFT calculations and found that La dopants attract protons and oxygen vacancies [13, 14]. Proton conductivity in Y-doped barium hafnate (BaHfO_3) has also been examined [15]. It has slightly higher proton conductivity than Y-doped barium zirconates (BaZrO_3) at high temperatures [15]. The conductivity at 773 K in air of $\text{BaY}_{0.1}\text{Hf}_{0.9}\text{O}_{3-\delta}$ and $\text{BaY}_{0.1}\text{Zr}_{0.9}\text{O}_{3-\delta}$ has

been found experimentally to be $\sim 10^{-2.9}$ and $\sim 10^{-3.5}$ S/cm, respectively [15]. The higher proton conductivity of doped BaHfO₃ can be a main advantage of using it as a proton conductor.

We showed previously that Ga-doping gives the highest chemical stability and La-doping gives the highest proton conductivity in BaZrO₃ among B-site doped BaZrO₃ [16]. We therefore examine in this paper the chemical stability and proton conductivity of Ga or La-doped barium stannate (BaSnO₃) and barium hafnate (BaHfO₃). In this paper, we examine the stability of doped BaSnO₃ and BaHfO₃ with respect to carbonate formation. We used DFT calculations of reaction free energies at finite temperatures, enabling us to predict the phase stability of oxide and carbonate phases as functions of temperature and CO₂ partial pressure. Then, the proton mobility through each material is investigated. Extensive DFT calculations are performed to elucidate the activation energies and hopping prefactors for local hops by protons, and this information is integrated into a lattice model for the doped material to determine net proton mobilities.

2. Calculation methods

Plane wave DFT calculations are performed for 0 K total energies of each compound with the Vienna *ab initio* Simulation Package (VASP) [17, 18]. For calculating the DFT total energy of each material we use the projector augmented wave (PAW) method to describe the core electrons of each atom. Electron exchange and correlation effects are described using the generalized gradient approximation (GGA) with the Perdew-Wang 91 (PW91) functional [17-19].

The energy cutoff for total energy calculations is 500 eV for all compounds. k -points are obtained using the Monkhorst-Pack method [20] with the number of k -points chosen to give a spacing of about $0.028 \text{ \AA}^{-1}$ along the axes of the reciprocal unit cells.

Experimental structures reported in the Inorganic Crystal Structure Database (ICSD) are used to start geometry optimization (the lattice parameters and atomic positions) in DFT calculations [21]. Geometry relaxations are done using a Conjugate Gradient algorithm until the forces on all unconstrained atoms are less than 0.03 eV/Å.

Additionally, we compute the temperature-dependent free energy of each solid for our studies of chemical stability. Calculations of the phonon density of states and the resulting vibrational contributions to the free energy for each material involved in a reaction were performed using the PHONON code implemented by Parlinski [22]. A displacement magnitude of 0.03 Å is chosen. 117 distinct displacement calculations were needed for each doped material. The undoped materials only required 4 displacement calculations each. The free energy of reaction at finite temperature, $\Delta G(T)$, can be computed within the harmonic approximation once the vibrational density of states for the material is known [23]. It is assumed that $\Delta(PV)_{solids} \ll (PV)_{CO_2}$. We treat gaseous CO₂ as an ideal gas. The free energies of CO₂ are obtained from [24]

$$G_{CO_2} = \frac{7}{2}RT + \sum_{i=1}^4 \frac{N_a h \nu_i}{e^{h \nu_i / kT} - 1} - TS_{CO_2}(T) , \quad (1)$$

where N_a is Avogadro's constant, R is the universal gas constant, T is temperature, and ν_i are the vibrational frequencies of CO₂ in G_{CO₂}. The experimental vibrational frequencies were used for CO₂ are 673, 1354, and 2397 cm⁻¹ for the π_u , σ_g^+ , and σ_u^+ modes, respectively. The entropy of CO₂ is accurately obtained by using the Shomate equation [25].

Instead of performing Nudged Elastic Band (NEB) calculations, which were used in other theoretical studies to find the transition states for proton transfer and rotation, an efficient way to find the transition states is employed [26-28]. When the initial estimated proton position at a transition state is close enough to its true value, this position tends toward the saddle point during a quasi-Newton optimization [26]. Vibrational frequency calculations of proton are

performed to determine whether the geometry optimization converges to a correct transition state instead of a local minima site on the energy surface. A saddle point of the energy surface gives two real frequencies and one imaginary frequency when only the proton's degrees of freedom are considered.

3. DFT optimized structures

For each compound we considered, the lattice parameters and atomic positions are optimized using DFT calculations with a single unit cell starting from the experimental structures listed in the Inorganic Crystal Structure Database (ICSD) [21]. We study a single step decomposition mechanism for perovskites in the presence of CO₂. By assuming that the increase of partial pressure of CO₂ is low during the process, we are able to neglect subsequent decomposition reactions.

The optimized lattice constants for each compound are presented in Table 1 along with the corresponding experimental data. The initial structures for geometry relaxations are obtained from the experimental data available from the ICSD [21]. The predicted values using the GGA functional are mostly slightly larger than experimental lattice constants. Scheffler and co-workers have attributed the tendency of GGA to slightly overpredict lattice constants to an overestimation of repulsive core-valence exchange-correlation in GGA [29].

Table 1. Comparison of the experimental [21] and the DFT calculated structural parameters for the 8 crystalline compounds considered in our calculations, with all lengths in Å and angles in degrees.

Compound	Space group	Structural Parameters (Å, degree)	
		Experimental	Calculated
SnO ₂	<i>P42/MNM</i>	$a = 4.733$ $c = 3.182$	$a = 4.820$ $c = 3.240$
HfO ₂	<i>P12₁/c1</i>	$a = 5.113$ $b = 5.172$ $c = 5.295$ $\beta = 99.188$	$a = 5.123$ $b = 5.188$ $c = 5.294$ $\beta = 99.716$
Ga ₂ O ₃	<i>C12/m1</i>	$a = 12.230$ $b = 3.040$ $c = 5.800$ $\beta = 103.7$	$a = 12.464$ $b = 3.096$ $c = 5.905$ $\beta = 103.8$
La ₂ O ₃	<i>P-3m1</i>	$a = 3.940$ $b = 3.940$ $c = 6.130$ $\gamma = 120$	$a = 3.939$ $b = 3.939$ $c = 6.149$ $\gamma = 120$
Y ₂ O ₃	<i>Ia-3</i>	$a = 10.611$	$a = 10.694$
BaCO ₃	<i>Pnma</i>	$a = 6.434$ $b = 5.315$ $c = 8.904$	$a = 6.582$ $b = 5.364$ $c = 9.003$
BaSnO ₃	<i>Pm-3m</i>	$a = 4.156$	$a = 4.181$
BaHfO ₃	<i>Pm-3m</i>	$a = 4.171$	$a = 4.194$

4. Chemical stability

The carbonate formation reactions of M₂-doped Ba(M₁)O₃ in the presence of CO₂ can be described as

where M₂ is a trivalent dopant such as Ga, La, or Y, and M₁ is a B-site host species, such as Hf or Sn. We investigate the stability of undoped-Ba(M₁)O₃, and extend our calculations to materials doped with M₂³⁺ at the B-site. With the introduction of dopants, oxygen vacancies are

formed to ensure charge neutrality [30]. The dopant concentration used in our calculations is 2/8 (25%). Thus, the net stoichiometry of the doped materials is $\text{Ba}_8(\text{M}_1)_6(\text{M}_2)_2\text{O}_{23}$. The $2 \times 2 \times 2$ unit cells are utilized for doped $\text{Ba}(\text{M}_1)\text{O}_3$ in the computational supercell, so each supercell contain two (one) dopant atoms (O vacancy). The arrangement with the lowest energy is employed for calculation of the VDOS. For Ga, this state has two dopant atoms placed next to each other in three of the perovskites we investigate, whereas the two dopants in the lowest energy state are separated by 6.27, and 7.53 Å for La in BaHfO_3 , and BaSnO_3 , respectively.

We also considered the configurational entropy of disordered M_2^{3+} and oxygen vacancies to compute the free energy of doped materials [31]. The configurational entropy comes from the Boltzmann definition of entropy, $S = k \ln \Omega$, where Ω is the number of configurations of dopants and vacancies possible [32]. If we assume all orderings of dopants and vacancies are equally likely, this gives a configurational entropy for $\text{BaSn}_{0.75}(\text{M}_2)_{0.25}\text{O}_{3-\delta}$, and $\text{BaHf}_{0.75}(\text{M}_2)_{0.25}\text{O}_{3-\delta}$ of $54.1 \text{ J K}^{-1} \text{ mol}^{-1}$. Because there are small energy differences between many configurations, this is likely to be an overestimation of the true configurational entropy. This effect is not explored further. The consequences of considering configurational entropy in a more detailed way have been explored by Fuks *et al.* [33] and these methods could be adapted to the materials we considered in the future.

The equilibrium condition for carbonate formation follows a van't Hoff relation:

$$\frac{P_{\text{CO}_2}}{P_0} = \exp\left(\frac{\Delta G}{RT}\right), \quad (3)$$

$$\Delta G(T) = \Delta E_0 - n_1 G_{\text{CO}_2}(T) + \Delta F^{\text{solids}}(T), \quad (4)$$

where ΔE_0 is the difference of ground state electronic total energy determined using DFT between the reactants and products, ΔG is Gibbs free energy difference between the reactants and products, n_1 is the number of moles of CO_2 involved in the reaction, G_{CO_2} is a free energy of

CO_2 , ΔF^{solids} is the vibrational free energy change between the solids of products and reactants, R is the gas constant, T is the temperature, and P_0 is the standard state reference pressure.

The equilibrium CO_2 pressure associated with carbonate formation of undoped and doped $\text{Ba}(\text{M}_1)\text{O}_3$ as predicted by our calculations is shown in Figure 1 and Figure 2, using $P_0 = 1$ bar. We define T^* to be the critical temperature at which carbonate formation becomes favorable. We provide results at a CO_2 pressure of 1 bar, as every material examined depends on CO_2 pressure in an identical manner. Among a set of materials, perovskites with higher critical temperatures are more prone to carbonate formation and are less chemically stable.

Fig. 1: van't Hoff plot for the carbonate formation reaction of undoped $\text{Ba}(\text{M}_1)\text{O}_3$, $\text{Ba}(\text{M}_1)\text{O}_3 + \text{CO}_2 \leftrightarrow \text{BaCO}_3 + (\text{M}_1)\text{O}_2$ for $\text{M}_1 = \text{Hf}$ or Sn . The horizontal dashed line indicates $P_{\text{CO}_2}/P_0 = 1$.

Fig. 2: van't Hoff plot for the carbonate formation reaction of M_2 -doped $Ba(M_1)O_3$, $Ba_8(M_1)_6(M_2)_2O_{23} + 8CO_2 \leftrightarrow 8BaCO_3 + 6(M_1)O_2 + (M_2)_2O_3$ for $M_1 = Hf$ or Sn and $M_2 = Ga$ or La . The horizontal dashed line corresponds to $P_{CO_2}/P_0 = 1$.

Fig. 3: Free energy of reaction, ΔG , as a function of temperature for carbonate formation reaction for undoped materials, $Ba(M_1)O_3 + CO_2 \leftrightarrow BaCO_3 + (M_1)O_2$ for $M_1 = Hf$ or Sn .

Fig. 4: Free energy of reaction, ΔG , as a function of temperature for carbonate formation reactions for doped BaHfO_3 and BaSnO_3 . The results for the doped materials correspond to the reaction $\text{Ba}_8(\text{M}_1)_6(\text{M}_2)_2\text{O}_{23} + 8\text{CO}_2 \leftrightarrow 8\text{BaCO}_3 + 6(\text{M}_1)\text{O}_2 + (\text{M}_2)_2\text{O}_3$ for $\text{M}_1 = \text{Hf}$ or Sn and $\text{M}_2 = \text{Ga}$ or La .

Figures 3 and 4 describe the stability of the undoped and doped materials examined, respectively, at a CO_2 pressure of 1 bar. The rank of the chemical stability of undoped- $\text{Ba}(\text{M}_1)\text{O}_3$ with respect to CO_2 is $\text{M}_1 = \text{Hf}$ ($T^* = 664 \text{ K}$) $>$ Sn ($T^* = 794 \text{ K}$), as seen in Figure 3. The calculated critical temperature of undoped BaZrO_3 in our previous study was $T^* = 688 \text{ K}$, which is lower than the critical temperature of undoped BaSnO_3 and higher than undoped BaHfO_3 's critical temperature [16]. Among the materials we investigate, BaHfO_3 shows the highest chemical stability (i.e., the lowest critical temperature). The rank of the chemical stability of M_2 -doped $\text{Ba}(\text{M}_1)\text{O}_3$ with respect to CO_2 is $\text{Ga-doped BaHfO}_3 > \text{Ga-doped BaSnO}_3 > \text{La-doped BaSnO}_3 > \text{La-doped BaHfO}_3$. Previously, we found the critical temperature of Ga-doped BaZrO_3 and La-doped BaZrO_3 was $T^* = 786 \text{ K}$ and 936 K , respectively [16]. As seen in table 2, doped

BaHfO₃ has lower critical temperature /higher chemical stability than doped BaZrO₃ in both Ga and La doping [16]. It is also clear from these results that the Ga-doped perovskite is more stable against carbonate formation reaction than La-doped perovskites.

Table 2: Predicted critical temperature of Ba₈(M₁)₆(M₂)₂O₂₃ for M₁ = Hf or Sn, and M₂ = Ga or La.

Material	T* (K)	Material	T* (K)	Material	T* (K)
BaHfO ₃	664	Ga-BaHfO ₃	772	La-BaHfO ₃	933
BaSnO ₃	794	Ga-BaSnO ₃	871	La-BaSnO ₃	882

Table 3: The difference of critical temperature between M₂-Ba(M₁)O₃ and Ba(M₁)O₃ for M₁ = Hf or Sn, and M₂ = Ga or La.

Dopant	Material	Δ T* (K)
Ga	BaHfO ₃	108
Ga	BaSnO ₃	77
La	BaHfO ₃	269
La	BaSnO ₃	88

Table 3 summarizes the change in critical temperature associated with the dopants we examine. The Ga dopant induces a smaller increase of critical temperature than the La dopant in the materials we examine. The critical temperature of doped BaSnO₃ does not vary significantly with the presence of dopants. As such, the chemical stability of BaSnO₃ is not very sensitive to different dopants. To summarize the results of this section, our calculations show that adding La or Ga to stannate, or hafnate decreases the chemical stability of these materials.

5. Proton conductivity

In our DFT calculations, one Sn⁴⁺ or Hf⁴⁺ ion in a simulation volume of 2×2×2 unit cells is doped by a trivalent dopant (M₂)³⁺. The dopant concentration in our system is therefore 1/8 (12.5%). Once a proton is introduced, the doped simulation volume becomes charge neutral [34].

In this volume, we designate seven (three) representative environments that possess different energy barriers for proton transfer (proton rotation) for B-site doped $\text{Ba}(\text{M}_1)\text{O}_3$. In our analysis, it is assumed that the environment related to each proton hopping is described using the nearest neighbors of the initial and final sites of the proton.

For B-site doped $\text{Ba}(\text{M}_1)\text{O}_3$, we computed the energy barriers for the 10 proton hops using DFT for Ga- or La-doped- BaSnO_3 and BaHfO_3 . These hops and energy barriers are listed in the Appendix. There are two real vibrational frequencies and one imaginary vibrational frequency at the transition state when only the proton is relaxed and the other atoms are fixed.

Proton conductivity is highly dependent upon the presence of dopants. Undoped BaZrO_3 is chemically stable, but exhibits low proton conductivity [35]. The impact of Ga and La dopants on proton conductivity is significant. In our previous studies of M_2 -doped- BaZrO_3 , La-doped BaZrO_3 shows the highest proton conductivity among the materials we investigated [16]. From this previous work, we find that the contribution of formation energy to proton conductivity is larger than the contribution of proton diffusivity. In this section, we study proton conductivity in Ga- or La-doped BaSnO_3 and BaHfO_3 . For each material, DFT calculations are performed to obtain the relevant proton hopping energy barriers and then subsequently Kinetic Monte Carlo (KMC) simulations are employed to provide the overall diffusivity of protons.

Using Harmonic Transition State Theory, we determined the hopping rate for each event after computing the proton vibrational frequencies with DFT [36]. After the proton hopping rates are defined, proton diffusivities in M_2 -doped $\text{Ba}(\text{M}_1)\text{O}_3$ were obtained with KMC. In our KMC simulations, we let a simulation volume of an alloy consist of randomly arranged atoms with the desired trivalent dopant composition. We use a simulation volume of $5 \times 5 \times 5$ unit cells. A simple algorithm describing the hopping dynamics of protons correctly reproduces the local

hopping rates [36]. At each time step a proton and its move direction are randomly selected. Acceptance of a proton hop is determined by a probability given by the ratio of the attempted proton hopping rate to the maximum proton hopping rate. Time increments by $(4 k_{\text{fast}} N_{\text{H}^+})^{-1}$, where N_{H^+} is the number of protons in the simulation volume and k_{fast} is the fastest hopping rate. An Einstein expression relating diffusivity to mean square displacement governs the overall proton self diffusivity [37, 38]. The mean square displacement increases linearly with time and the slope describes the diffusion coefficient.

Table 4: Effective activation energy and pre-exponential factor of the materials we investigated.

Material	E_d (eV)	A ($\text{cm}^2 \text{s}^{-1}$)	Material	E_d (eV)	A ($\text{cm}^2 \text{s}^{-1}$)	Material	E_d (eV)	A ($\text{cm}^2 \text{s}^{-1}$)
BaHfO ₃	0.233	1.48×10^{-5}	La-BaHfO ₃	0.244	1.33×10^{-5}	Ga-BaHfO ₃	0.568	2.23×10^{-5}
BaSnO ₃	0.294	2.24×10^{-5}	La-BaSnO ₃	0.314	2.26×10^{-5}	Ga-BaSnO ₃	0.58	2.13×10^{-5}

Table 4 shows calculated values for the effective activation energy and pre-exponential factor for proton diffusion in each doped material. In undoped and doped (Ga or La) material, BaHfO₃ showed the lower effective energy barrier than BaSnO₃. Using Ga, a small dopant, significantly increases the diffusion activation energy relative to the undoped materials. Using La, a large dopant, however, does not significantly impact the diffusion activation energy. The difference of the pre-exponential factors between materials are less than one order magnitude. This is consistent with the trend that we see in B-site doped in BaZrO₃, where the smaller dopants lead to higher energy barriers for proton diffusion due to the strong bonds with protons in the material [16, 39].

To complement the information we report above regarding the proton diffusivity, it is also important to understand the proton concentration, which also contributes to the proton conductivity. For the comparison of materials, the methods described in the earlier studies of B-

site doped BaZrO₃ are used [16]. As discussed in our previous work, it is useful to use the ratio of proton conductivities rather than to use the absolute quantity in comparing the relative properties of materials [16]. The ratio of the proton conductivities for two materials is [16]

$$\frac{\sigma_1}{\sigma_2} = \frac{C_1 D_1}{C_2 D_2} = \frac{N_1 A_1}{N_2 A_2} \exp \left[-\frac{(\Delta E_f + \Delta E_d)}{kT} \right], \quad (5)$$

where C is the proton concentration at thermodynamic equilibrium, D is proton diffusivity, N is the number of possible proton binding sites, A is a pre-exponential factor, E_f is the formation energy of a proton, E_d is the effective activation energy, and k is the Boltzmann constant. We choose Y-doped BaZrO₃ as a reference state with the subscript 1, referring to the Y-doped material, because it is the most commonly used dopant. This allows us to clearly see the effects of different dopants (e.g., Ga and La) on proton conductivity. For example, when σ_1/σ_2 is smaller than 1, material 2 yields a higher conductivity than Y-doped BaZrO₃. Our results for all doped materials we consider are shown in Table 5.

Table 5: Summary of the proton conductivity of M₂-doped materials relative to Y-doped BaZrO₃ (σ_1/σ_2) at T = 600 K. All energies are shown in eV.

	ΔE_f	ΔE_d	A_1/A_2	σ_1/σ_2
La-BaHfO ₃	0.638	0.041	1.44	2.90×10^{-6}
La-BaSnO ₃	0.53	-0.03	0.843	5.20×10^{-5}
Ga-BaHfO ₃	-0.232	-0.283	0.854	18105
Ga-BaSnO ₃	-0.274	-0.295	0.895	53718

Our results in Tables 2 and 5 rank the chemical stabilities of the doped materials as Ga-doped BaHfO₃ > Ga-doped BaSnO₃ > La-doped BaSnO₃ > La-doped BaHfO₃ while the rank for proton conductivity at 600 K is La-doped BaHfO₃ > La-doped BaSnO₃ > Ga-doped BaHfO₃ > Ga-doped BaSnO₃, respectively. Ga-doping shows higher chemical stability while La-doping shows higher proton conductivity for these two perovskites, BaHfO₃ and BaSnO₃. This is

associated with the high electronegativity of Ga and the large ionic radius of La. Because 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.

La dopants show lower electronegativity than Ga dopants, demonstrating that La-doping leads to unstable perovskites. The chemical stability of BaSnO_3 is not very susceptible to the dopants used, whereas the proton conductivity of BaSnO_3 is very sensitive to the dopants used. In other words, there is a clear difference of proton conductivity between Ga-doped BaSnO_3 and La-doped BaSnO_3 . However, the difference of the critical temperature describing the chemical stability of the perovskites is smaller between Ga-doped BaSnO_3 and La-doped BaSnO_3 than between Ga-doped BaZrO_3 (BaHfO_3) and La-doped BaZrO_3 (BaHfO_3).

Fig. 5: $\Delta E_f + \Delta E_d$ (eV) as a function of critical temperature T^* (K) of dopants in doped M_2 -doped $\text{Ba}(\text{M}_1)\text{O}_3$. The red line corresponds to the critical temperature of Ga-doped BaZrO_3 , and the blue line refers to the $\Delta E_f + \Delta E_d$ value of La-doped BaZrO_3 from reference [16].

One of our goals is to compare chemical stability and proton conductivity of Ga- or La-

doped BaSnO₃ and Ga- or La-doped BaHfO₃ with Ga- or La-doped BaZrO₃. In our previous studies, $\Delta E_f + \Delta E_d$ of Ga-doped BaZrO₃ and La-doped BaZrO₃ was -0.457 and 0.489, and the T^* of Ga-doped BaZrO₃ and La-doped BaZrO₃ was 786 K and 936 K, respectively [16]. These values are also included in Figure 5 to compare the chemical stability and proton conductivity of doped BaZrO₃ with BaHfO₃ and BaSnO₃.

In Figure 5, there is a clear tradeoff between chemical stability and proton conductivity in doped BaHfO₃, BaSnO₃, and BaZrO₃. However, the effects of doping on the chemical stability of BaSnO₃ are small. For conductivity, both La-doped BaHfO₃ and La-doped BaSnO₃ show higher proton conductivity than La-doped BaZrO₃. We find that the highest stability is for Ga-doped BaHfO₃ while the highest proton conductivity is for La-doped BaHfO₃.

Ga-doped BaHfO₃ shows the highest chemical stability and La-doped BaHfO₃ shows the highest proton conductivity among the materials examined. BaSnO₃ is not sensitive to the dopants for chemical stability compared to the other two materials, BaHfO₃ and BaZrO₃.

6. Summary

In this paper, we use promising dopants found in our previous studies on M₂-doped BaZrO₃ for chemical stability (Ga) and proton conductivity (La) using DFT-based modeling in two different kinds of materials, BaSnO₃ and BaHfO₃. We conclude that there exists an inherent tradeoff between chemical stability and proton conductivity in both doped BaSnO₃ and BaHfO₃. We find that doped BaHfO₃ is promising to study further in a co-doped case, because the highest stability is found in Ga-doped BaHfO₃ and the highest proton conductivity is observed in La-doped BaHfO₃.

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Appendix: Energy Barriers for Proton Diffusion

Table A.1: Energy barriers of the proton in the case where a dopant is a nearest neighbor of the initial or final proton and the distance (d_{O-O}) between the two O closest to the migrating proton, where $M_1 = \text{Hf}$ or Sn , $M_2 = \text{Ga}$ or La .

	Nearest Neighbor of Initial Proton	Nearest Neighbor of Final Proton	E_a (eV), d_{O-O} (Å)							
			M_1	M_2	M_1	M_2	M_1	M_2	M_1	M_2
			Hf	Ga	Hf	La	Sn	Ga	Sn	La
T 1	M_2, M_2	M_2, M_2	0.28, 2.453		2.16, 2.320		0.38, 2.448		1.86, 2.318	
T 2	M_1, M_2	M_1, M_2	0.20, 2.462		0.38, 2.408		0.22, 2.438		0.56, 2.420	
T 3	M_1, M_2	M_2, M_2	0.08, 2.450		1.41, 2.367		0.15, 2.451		0.64, 2.359	
T 4	M_2, M_2	M_2, M_1	0.34, 2.450		0.98, 2.367		0.44, 2.451		0.22, 2.359	
T 5	M_2, M_1	M_1, M_1	0.69, 2.464		0.44, 2.363		0.68, 2.433		0.10, 2.364	
T 6	M_1, M_1	M_1, M_2	0.13, 2.464		0.62, 2.363		0.17, 2.433		0.55, 2.364	
T 7	M_1, M_1	M_1, M_1	0.26, 2.444		0.26, 2.444		0.33, 2.410		0.33, 2.410	
R 1	M_2, M_2	M_2, M_2	0.13		2.61		0.18		2.07	
R 2	M_1, M_2	M_1, M_2	0.18		0.70		0.19		0.51	
R 3	M_1, M_1	M_1, M_1	0.17		0.17		0.21		0.21	

References

- [1] H. Iwahara, T. Esaka, H. Uchida, N. Maeda, *Solid State Ionics* 3 (1981) 359-363.
- [2] H. Iwahara, in: *Solid State Ionics*, eds. M. Balkanski, T. Takahashi and H.L. Tuller (Elsevier, Amsterdam, 1992) pp. 575-586.
- [3] T. Norby, Proton conductivity in perovskite oxides, in *Perovskite oxide for solid oxide fuel cells*, Springer, 2009, 217.
- [4] K. D. Kreuer, *Annu. Rev. Mater. Res.* 33 (2003) 333-359.
- [5] K. M. Nicholson, D. S. Sholl, *Phys. Rev. B* 86 (2012) 134113.
- [6] B. Amin, N. Singh, T. M. Tritt, H. N. Alshareef and U. Schwingenschlögl, *Appl. Phys. Lett.* 103, (2013) 031907.
- [7] Z. Ali, Iftikhar Ahmad, B. Amin, M. Maqbool, G. Murtaza, I. Khan, M.J. Akhtar, F. Ghaffor, *Physica B: Condensed Matter*, 406 (2011) 3800.
- [8] R. Mukundan, E. L. Brosha, S. A. Birdsell, A. L. Costello, F. H. Garzon, R. S. Willms, *J. Electrochem. Soc.* 146 (1999), 2184-2187.
- [9] B. Ostrick, M. Fleischer, U. Lampe, H. Meixner, *Sensors Actuat. B Chem.* 44 (1997) 601-606.
- [10] K. D. Kreuer, *Solid State Ionics* 125 (1999) 285-302.
- [11] P. Murugaraj, K. D. Kreuer, T. He, T. Schober, J. Maier, *Solid State Ionics* 98 (1997) 1-6.
- [12] T. Schober, *Solid State Ionics* 109 (1998) 1-11.
- [13] E. Bevilion, G. Geneste, A. Chesnaud, Y. Z. Wang, G. Dezanneau, *Ionics* 14 (2008) 293-301.
- [14] E. Bevilion, A. Chesnaud, Y. Z. Wang, G. Dezanneau, G. Geneste, *J. Phys.: Condens. Matter* 20 (2008) 145217.
- [15] F. M. M. Snijkers, A. Buekenhoudt, J. J. Luyten, J. Cooymans, M. Mertens, *Scr. Mater.* 51 (2004) 1129-1134.
- [16] S. G. Kang, D. S. Sholl, *RSC Adv.* 3 (2013) 3333-3341.
- [17] G. Kresse, J. Hafner, *Phys. Rev. B* 47 (1993) 558.
- [18] G. Kresse, J. Furthmüller, *Phys. Rev. B* 54 (1996) 11169.
- [19] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* 46 (1992) 6671.
- [20] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* 13 (1976) 5188.
- [21] The Inorganic Crystal Structure Database (ICSD). The Inorganic Crystal Structure Database (ICSD) <http://www.fiz-informationsdienste.de/en/DB/icsd/>.
- [22] K. Parlinski, Software PHONON, 2005.
- [23] G. J. Ackland, *J. Phys.: Condens. Matter* 14 (2002) 2975-3000.
- [24] R. G. Mortimer, *Physical Chemistry*. 2nd ed., (Academic Press, New York, 2000).
- [25] M. J. W. Chase, *J. Phys. Chem. Ref. Data Monogr.* 9 (1998) 1.
- [26] S. Q. Hao, D. S. Sholl, *Energy Environ. Sci.*, 1 (2008) 175-183.
- [27] S. Q. Hao, M. Widom and D. S. Sholl, *J. Phys.: Condens. Matter*, 11 (2009) 21.
- [28] S. Q. Hao and D. S. Sholl, *J. Member. Sci.*, 381 (2011) 192-196.
- [29] M. Fuchs, M. Bockstedte, E. Pehlke, M. Scheffler, *Phys. Rev. B* 57 (1998) 2134.
- [30] K. D. Kreuer, W. Munch, M. Ise, T. He, A. Fuchs, U. Traub, J. Maier, *Ber. Bunsen. Phys. Chem.* 101 (1997) 1344-1350.
- [31] K. C. Kim, D. S. Sholl, *J. Phys. Chem. C* 114 (2010) 678-686.

- [32] J. W. Chamberlain, D. M. Hunten, Theory of Planetary Atmospheres: An Introduction to Their Physics and Chemistry (Academic Press, San Diego, 1987).
- [33] D. Fuks, L. Bakaleinikov, E. A. Kotomin, J. Felsteiner, A. Gordon, R. A. Evarestov, D. Gryaznov, J. Maier, Solid State Ionics 177 (2006) 217-222.
- [34] M. A. Gomez, M. Chunduru, L. Chigweshe, L. Foster, S. J. Fensin, K. M. Fletcher, L. E. Fernandez, J. Chem. Phys. 132 (2010) 214709.
- [35] Z. Zhong, Solid State Ionics 178 (2007) 213-220.
- [36] D. S. Sholl, J. A. Steckel, Density Functional Theory: A Practical Introduction (Wiley, Hoboken, NJ, 2009).
- [37] P. Kamakoti, D. S. Sholl, Phys. Rev. B 71 (2005) 014301.
- [38] L. Semidey-Flecha, D. S. Sholl, J. Chem. Phys. 128 (2008) 144701.
- [39] M. S. Islam, S. J. Stokes, J. Mater. Chem., 20 (2010) 6258-6264.