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#### **Executive Summary**

Within the ECOLEFINS project, supported by the Horizon Europe Innovation Council's EIC Pathfinder program, we aim to develop a novel all-solid-state electrolysis device, capable of converting water and CO<sub>2</sub> gas into light olefins and oxygen. For the targeted electrochemical process, it is necessary to use an electrolyte capable of simultaneous oxygen ion and proton transport at intermediate temperatures (350°C-450°C). In this document, we describe our midterm progress on the computer assisted material design of possible novel co-ionic electrolytes suitable for this task.

For this purpose, we employ ab initio methods to simulate the material properties of candidate compositions from an atomistic model, without the need for experimental data. This is used to provide insights into the (atomistic) structural properties, electronic structure, and transport properties of reference materials and compare them to those of novel material compositions with potentially desired properties through substitution or doping of reference materials.

Our results focus on two material classes: i) the classical proton conducting perovskites based on barium cerate (BCO) – barium zirconate (BZO) solid solution and ii) the disordered hexagonal perovskite  $Ba_7Nb_4MoO_{20}$  (BNM). Furthermore, we have explored and developed methods to model grain boundary segregation, and transport properties. The latter is achieved through the application of the recently developed machine learned force field (ML-FF) approach, significantly reducing computational resources, while allowing for improved data analysis.

The computationally proposed materials in this Task 1.1 might help developing sustainable alternative production technologies, for the production of carbon neutral light olefins.





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#### 1. Overview

#### 1.1. Methods of atomistic scale modeling

At first, we need to obtain the atomistic configurations of the material. We can start with crystallographic data of base materials and (if necessary) introduce partial site occupancies of the desired substitutes. Since modeling of substitutions needs partial occupancies of atomic sites in large supercells of the base lattice, the large number of possible atomistic configurations can lead to a rapid explosion of the combinatorics. For example, to model  $Ba_{1.0}Zr_{0.75}Y_{0.25}O_{2.875}$ , we need to introduce 25% fractional occupancy of Y at the B (Zr) site as well as 2.875/3 occupancy of O at oxygen sites. In a 4x4x4 supercell, this means we have to evaluate the energies for 10<sup>28</sup> configurations. Due to the computational cost of DFT calculations, we first use Coulomb energy calculations, to find favorable ones. For systems with up to 10<sup>15</sup> possible configurations, a brute force approach implemented in the Supercell code [1] has been used to calculate the energies of all configurations. For systems with more complex configurations, we now employ our newly developed GOAC package [2], which allows systems with up to  $10^{1000}$  possible configurations using a heuristics-based approach. From the Coulomb calculations, we then choose promising candidate configurations and perform DFT calculation to obtain total energies and optimized geometries that will be discussed in the following.

To study the atomistic and electronic structure of materials, DFT calculation with PBE and HSE06 functionals was used, respectively. Ab initio molecular dynamics (AIMD) is used to compute the self-diffusivity. Density functional perturbation theory (DFPT) and finite displacements (FD) allow insights into the vibrational properties. Instead of AIMD, we also apply the machine learning force field ML-FF method as implemented in VASP to reduce the computational cost of MD calculations [3], thereby allowing for longer simulation times and improved statistics, with only marginal loss of accuracy. For the study of grain boundaries, we employ the AIMSGB code, which generates grain boundary unit cells viable for calculations.

#### 1.2. Material development strategy

In order to develop new materials and guide the development of the co-ionic electrolyte, we are following two approaches: 1) We aim to develop novel ceramic electrolyte materials with promising intrinsic co-ionic conductivity such as the disordered hexagonal perovskite BNM (Ba<sub>7</sub>Nb<sub>4</sub>Mo<sub>1</sub>O<sub>20</sub>) with substitution at Ba and Nb sites with alkali and tetravalent transition metals, respectively, and 2) we are also investigating electrochemical properties of Barium-Zirconate-based proton conducting perovskites. Primarily, we study the electrochemical properties of BZCY ( $Ba_{1.0}Zr_{1.0-x-v}Ce_xY_vO_{3-\delta}$ ) and BZCS ( $Ba_{1.0}Zr_{1.0-x-v}Ce_xSc_vO_{3-\delta}$ ) to search for compositions which are sufficiently co-ionic, due to the intrinsic oxygen ion conductivity of the perovskites. Next, we aim to provide the insights on material compositions of proton-conductor BZCY for application in a cer-cer composite together with an established oxygen-ion conductor fluorite-type material such as GDC10 (Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub>).





#### 2. Results

#### 2.1. Novel disordered hexagonal perovskites Ba<sub>7-x</sub>A<sub>x</sub>Nb<sub>4-y</sub>Mo<sub>1</sub>M<sub>y</sub>O<sub>20-δ</sub> (A: K, Cs; M: Ti, Sn, Zr)

BNM is a new class of material, which has been synthesized and investigated by several experimentalist groups [4,5]. Ba<sub>7-x</sub>A<sub>x</sub>Nb<sub>4-</sub> <sub>v</sub>Mo<sub>1</sub>B<sub>v</sub>O<sub>20-δ</sub> (A=K, Cs; B=Ti, Sn, Zr) was studied in a 4x4x1 supercell containing 16 formula units. For each A and B, we introduced 2 dopant atoms (x=1.7%, y=2.5%), allowing for the creation of one additional oxygen vacancy. In this project, we started with the base stoichiometric composition Ba<sub>7</sub>Nb<sub>4</sub>MoO<sub>20</sub> and partially replaced Ba by K or Cs and Nb by Sn, Ti or Zr. These elements have been chosen based on good matching of their ionic radius as compared to Ba<sup>2+</sup> and Nb<sup>5+</sup>, respectively. The initial goal of this work was to explore the possibility of introducing additional oxygen vacancies in the central Nb layers that can lead to additional hydration concentration and transport channels for H<sup>+</sup> (Figure 1). Our combined Coulomb



Figure 1: Schematic of concept of the  $Ba_{7-x}A_xNb_{4-y}Mo_1M_yO_{20-6}$  (A=K, Cs; B=Ti, Sn, Zr) doping strategy. Partial substitution of  $Nb^{5+}$  by Ti<sup>4+</sup> introduces oxygen vacancies in the central Nb layers of the lattice, available for hydration and providing additional channels for H<sup>+</sup> transport.

DFT calculations show that for all investigated substitutions on Ba<sup>2+</sup> and transition metal sites additional oxygen vacancies are created in the central Nb rich layers. This is probably due to the lower energy cost for removing oxygen next to the lower charge state substituents.

We are now working on the calculations of hydration energies for most promising materials. Subsequently, we will investigate the ionic transport in the materials using *ab initio molecular dynamics (AIMD)* and/or ML-FF methods. Moreover, we aim to simulate grain boundary (GB) effects such as dopant segregation and

possible pathways for ionic transport at GBs. While the bulk co-ionic conductivity of BNM is promising, GB conductivity is comparatively poor, such that improvements on ionic transport across BNM GBs can improve the total conductivity of the material. We have recently performed a similar study on segregation of Y<sup>3+</sup>/Yb<sup>3+</sup> in BZY [6], which is also included in the second part of this report.

Table 1: Volume change for each studied dopant in  $Ba_{7-x}A_xNb_{4-y}Mo_1M_yO_{20-\delta}$ . For each configuration, two dopant atoms were introduced, allowing to introduce one oxygen vacancy.

| Lattice site | Dopant           | ΔV in % |
|--------------|------------------|---------|
| А            | K+               | 0.127   |
| А            | Cs+              | 0.133   |
| М            | Ti <sup>4+</sup> | 0.022   |
| М            | Zr <sup>4+</sup> | 0.201   |
| Μ            | Sn <sup>4+</sup> | 0.127   |





#### 2.2. Zr rich BZCS (BaZr<sub>0.825-x</sub>Ce<sub>0.185</sub>Sc<sub>x</sub>O<sub>3-δ</sub>)

Motivated by experimental work of our project partners at USTAN, we have worked on Sc-doped Barium Zirconate-Cerate solid solution BaZr<sub>0.825</sub>- $_{x}Ce_{0.185}Sc_{x}O_{3-\delta}$  (BZCS) and compared it to the established BaZr<sub>0.825-x</sub>Ce<sub>0.185</sub>Y<sub>x</sub>O<sub>3-δ</sub> (BZCY). The BaZr<sub>0.825-</sub> <sub>x</sub>Ce<sub>0.185</sub>M<sub>x</sub>O<sub>3-δ</sub> (M= Y, Sc; x=12.5%, 25%, 37.5%) compositions were modeled using a rhombohedral  $\sqrt{2} \times \sqrt{2} \times \sqrt{2}$  supercell containing 16 formula units. Structural relaxation calculations were performed using DFT-PBE for all compositions. A schematic of the atomistic structure of these materials is shown in Figure 2. Due to its smaller ionic radius, we expect significantly reduced chemical expansion and higher dopant solubility of Sc as compared to Y. At higher substituent concentration, we expect reduced relative maximum hydration ability, such that some intrinsic oxygen ion conductivity is preserved at operating conditions, allowing for co-ionic conductivity.

Figure 3 shows the computed lattice constants for  $BaZr_{0.825-x}Ce_{0.185}M_xO_{3-6}$  (M: Sc, Y). The results show a large lattice expansion for increasing Y dopant concentration, but a small decrease of lattice constants for increasing Sc content. This is consistent with the reported ionic radii values of Y and Sc [7].

To evaluate the hydration energy, we need to compute the hydration enthalpy as well as entropy (mainly vibrational contribution). The former can be estimated in a straight forward manner from DFT total





Figure 6: Computed mean lattice constants in BaZr\_{0.825-x}Ce\_{0.185}M\_xO\_{3-6} for x =12.5%-37.5% with Sc<sup>3+</sup> and Y<sup>3+</sup> dopants. The singular lattice constants for a<sup>1</sup> to a<sup>3</sup> are marked by the triangular markers.

energies as depicted in Figure 4, while the latter requires more expensive phonon calculations which we plan to implement during the second phase of the project. The current results show a decrease in hydration energy with increasing dopant concentration from 12.5% to 25%. This could be related to a favorable structure formed by the fully occupied oxygen sublattice. Overall, the data shows first evidence that hydration of BZCY is energetically more favorable compared to that of BZCS, probably leading to a higher oxygen vacancy concentration at operating conditions, and thereby increased oxygen ion conductivity in the latter case. Secondly, we report an increase in lattice volume with hydration for both dopants, where Y doping shows a higher expansion for 37.5% dopant concentration. For a more complete picture, the hydration enthalpies for 2<sup>nd</sup> (x=25%, 37.5%) and 3<sup>rd</sup> hydration (x=37.5%) will be computed as well.







Figure 9: Hydration enthalpies ( $H_{hyd}$ ) (left) and hydration-induced volume change  $\Delta V$  (right) as function of dopant (M) concentration x in  $BaZr_{0.825-x}Ce_{0.185}M_xO_{3-\delta}$ , (M:Sc, Y).

We are now working on obtaining the full hydration energy from dopant oxygen vacancies by investigating the vibrational properties of the hydrated as compared to the dry material. Furthermore, we aim to study the stability of various compositions in contact with  $CO_2$  and  $H_2O$ . We are currently developing a ML-FF for BZY that can be used to study  $H^+$  and  $O^{2-}$  transport in this material, and we aim to apply this method also for the more complex  $BaZr_{1-x-y}Ce_xM_yO_{3-\delta}$  system. Furthermore, we will investigate the effect the reduction of  $Ce^{4+}$  in  $BaZr_{1-x-y}Ce_xM_yO_{3-\delta}$  which is known to allow for additional water uptake, thereby increasing the conductivity of Ce-rich compositions [8].





#### 2.3. Ce rich BZCS (BaZr<sub>0.25</sub>Ce<sub>0.75-x</sub>Sc<sub>x</sub>O<sub>3-δ</sub>)

After first establishing that Sc doped BZCO shows better potential for co-ionic conductivity, we focused on higher Ce content compositions, namely  $BaZr_{0.25}Ce_{0.75-x}Sc_xO_{3-\delta}$  (BZCS)modeling similar to experimentally synthesized compositions by our project partners from St Andrews with x = 0.05, 0.15 and 0.25, which also show promising stability in CO<sub>2</sub> atmosphere.

As Ce and Zr have the same nominal charges, we had to follow the following two steps to find the minimum energy structures. First, energies of different BCSO configurations of a  $\sqrt{2} \times \sqrt{2} \times 2$  supercell were evaluated by Coulomb analysis using the Supercell code, where charges of +2, +4, +3, and -2 were applied for Ba, Ce, Sc and O, respectively. In a second step, partial occupations for the Ce<sup>+4- $\epsilon$ </sup> sites for the appropriate Zr<sup>+4+ $\Delta$ </sup> content were introduced in the most promising configurations from the first step. The resulting structures were further evaluated using DFT-PBE. Here we employed a  $\sqrt{2} \times \sqrt{2} \times 2$  supercell, sampled with

а Г-point centred kpoint mesh of  $1 \times 1 \times 2$ and energy cut-off of 520 eV as well as energy and force convergence criteria of 5.0×10<sup>-5</sup> eV and 1.0×10<sup>-2</sup> eV/Å, respectively, were applied. PAW pseudopotentials with valence electron configurations of 5s<sup>2</sup> 5p<sup>6</sup> 5d<sup>0.01</sup> 6s<sup>1.99</sup>, 2s<sup>2</sup> 2p<sup>4</sup>, 4s<sup>2</sup> 4p<sup>6</sup> 4d<sup>3</sup> 5s<sup>1</sup>, 4f<sup>1</sup> 5s<sup>2</sup> 5p<sup>6</sup> 5d<sup>1</sup> 6s<sup>2</sup>, 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>2</sup> 4s<sup>1</sup>, for Ba, O, Zr, Ce and Sc were used, respectively.



Figure 10: Computed most favorable atomic structures for BaCe<sub>0.5</sub>Zr<sub>0.375</sub>Sc<sub>0.125</sub>O<sub>3-6</sub> (a) and BaCe<sub>0.5</sub>Zr<sub>0.25</sub>Sc<sub>0.25</sub>O<sub>3-6</sub> (b) from side (top) and top view (bottom) of the employed  $\sqrt{2} \times \sqrt{2} \times 2$  supercell. The inset arrow illustrates one cubic lattice constant of the perovskite unit cell in the side view.

The most favorable structures from structural relaxations are depicted in Figure 5. Their hydration behavior was modelled by introducing the corresponding amount of H<sub>2</sub>O molecules at oxygen vacancies. The results are shown in Figure 6. The left panel shows the obtained lattice constants as compared to the Zr rich compositions and shows larger chemical contraction by the doping for the Ce rich compositions as compared to the Zr rich compositions. The center panel illustrates the relative lattice expansion by hydration for the studies Ce rich compositions as a function of hydration percentage. Here we observe larger hydration induced lattice expansion for 25% Sc content as compared to 12.5% Sc content. The right panel shows the hydration enthalpy results, which suggest that the hydration for 25% Sc is more favorable for half and full hydration as compared to the results for 12.5% Sc, respectively. The energy cost of the lattice expansion therefore must be compensated by additional factors.





In the next steps, we will extend our investigation to higher Sc content of 37.5%. Additionally, in order to validate our claims on hydration enthalpy, we will repeat the calculation of hydration enthalpies from different starting configurations in terms of proton positions. Finally, and most importantly, we will perform 3 sets of AIMD studies focusing on the influence of temperature, Sc dopant concentration and hydration, respectively, with the latter allowing insights into proton, oxygen ion and co-ionic transport for a given composition.



Figure 13: Left: Lattice constants for 50% and 18.75% Ce content at varying Sc concentration in BaCe<sub>1-x-y</sub>Zr<sub>x</sub>Sc<sub>x</sub>O<sub>3-6</sub>. Center: Relative lattice expansion of BaCe<sub>0.5</sub>Zr<sub>0.5-x</sub>Sc<sub>x</sub>O<sub>3-6</sub> for x = (12.5%, 25%). Left: Preliminary calculated hydration enthalpies for BaCe<sub>0.5</sub>Zr<sub>0.5-x</sub>Sc<sub>x</sub>O<sub>3-6</sub> for x = (12.5%, 25%).





#### 2.4. Y and Yb doped BZO

#### 2.4.1. Dopant segregation at grain boundaries

To study Grain boundary and ionic transport in complex materials of this project, namely BZCY, BZCS, and BNM, we had to first develop our models and simulation approaches for simpler systems such as BaZr<sub>1.0-</sub>  $_xM_xO_{3-\delta}$ . BaZr<sub>1.0-x</sub>M<sub>x</sub>O<sub>3-\delta</sub> (M=Y/Yb). Grain boundary (GB) models were constructed by using Aimsgb [10] employing 48 formula units of BZO containing two identical grain boundaries due to periodic boundary conditions. We first started to find the most favourable sites for two oxygen vacancies and four Y/Yb ions in a  $\Sigma_{3}[110]/(-112)$  GB by performing Coulomb energy calculations on 2003395680 (2.0×10<sup>9</sup>) possible combinations applying the Supercell code [11]. We used charges of 2+ for Ba, 4+ for Zr, 3+ for Y/Yb and 2for oxygen. To model the SPS-sintered GB, a similar approach was utilized. To accommodate Y/Yb ions in the bulk region of our GB model, we artificially introduced two fixed trivalent ions next to the optimal oxygen vacancy position at the GB to repel four Y/Yb ions from the GB plane. To maintain the charge neutrality for this case, we reduced the Zr valence to +3.952 in this step. Subsequently, the artificially added trivalent ions at the GB plane were replaced by Zr ions. The resulting models are depicted in Figure 7. To calculate the segregation energy, which is the total energy difference between Y/Yb at the GB plane and bulk region  $(E_{Y/Yb}(GB) - E_{Y/Yb}(Bulk))$ , we performed spin-polarized DFT [12,13] calculations as implemented in the Vienna Ab initio Simulation Package (VASP) code [14] using the PBE functional [15] and the Projector Augmented-Wave (PAW) method [16]. A  $\Gamma$ -point centred k-point mesh of 2×1×4 and energy cut-off of 520 eV as well as energy and force convergence criteria of 5.0×10<sup>-5</sup> eV and 1.0×10<sup>-2</sup> eV/Å, respectively, were applied. Ionic positions and unit cell volume were fully optimized while the unit cell shape was fixed (ISIF=8). PAW pseudopotentials with valence electron configurations of 5s<sup>2</sup> 5p<sup>6</sup> 5d<sup>0.01</sup> 6s<sup>1.99</sup>, 2s<sup>2</sup> 2p<sup>4</sup>, 4s<sup>2</sup> 4p<sup>6</sup> 4d<sup>3</sup> 5s<sup>1</sup>, 4s<sup>2</sup> 4p<sup>6</sup> 4d<sup>2</sup> 5s<sup>1</sup>, and 5p<sup>6</sup> 5d<sup>1</sup> 6s<sup>2</sup> for Ba, O, Zr, Y and Yb were used, respectively.

Study of dopant segregation in the grain boundaries of barium zirconate ceramics is very important. The segregation can drastically influence the proton conductivity of these materials. In this work, we studied segregation of Y and Yb dopants in these materials using DFT together with our experimentalist partners performing HR-STEM measurements. Our calculations confirmed (using electrostatic analysis and density functional theory (DFT)) the segregation of both Y and Yb cations from bulk sites to grain boundary sites. The segregation energies in a representative GB model simulating a symmetric  $\Sigma3$  [110]/(-112) tilt GB for Y and Yb cations are calculated as -0.89 and -1.00 eV/atom, respectively. The segregation energies for Y and Yb are much larger than that calculated by A. Lindmann et al. [9] for Y without having oxygen vacancy at the



Figure 16:  $\Sigma_3[110]/(-112)$  grain boundary model. S1<sup>seg</sup> atomic positions correspond to atomic positions of Y/Yb dopants after segregation, while S2<sup>bulk</sup> are the atomic positions for the dopants used to simulate the non-equilibrium SPS state. The given V<sub>0</sub><sup>••</sup> positions are approximated from geometry change after oxygen vacancy introduction. Atomic visualizations were obtained using the VESTA suite.





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GB (-0.32 eV). This is because the clustering of oxygen vacancies with Y<sup>3+</sup>/Yb<sup>3+</sup> cations is electrostatically more favourable than that with  $Zr^{4+}$ . This result shows that oxygen vacancies clearly increase the driving force for Y/Yb segregation. This work has been already published in a high impact factor journal (Advanced Energy Materials: IF: 24.4) [6].

#### 2.4.2. Development of Machine learned force fields for study of proton transport properties

To evaluate the proton conductivity in  $BaZr_{0.75}Y_{0.25}O_{3-\delta}$  we applied Machine learned Force fields (ML-FF) trained on ab initio molecular dynamics (AIMD) data [17,18]. In order to study the ionic transport in solids, there are two *ab initio* methods routinely employed, namely *ab initio* molecular dynamics [19, 20] and the nudged elastic bands (NEB) method [21]. The first allows directly simulates ionic motion at femtosecond scale using a DFT framework, whereas the second uses a DFT approach to study non-equilibrium positions along a given transport path, allowing to directly calculate the transport barrier along that path. For the purpose of studying protonic motion in the materials of interest such as Barium Zirconates and Cerates, both supplementary methods AIMD [21] and NEB [22] (and successive methods [23,24]) have already been employed successfully to gain insights into how protons move within the ionic lattices. However, both methods have their limitations. For AIMD crucially, the computational cost is quite significant and without repeated measurements from the statistical method, errors are expected to be high. Oftentimes, simulation times are therefore at or below the 100ps range, and therefore do not reflect on transport on longer, nanosecond, timescale processes and are performed at unphysically high temperatures up to 1500°C [26,27]. Using ML-FFs, we aim to drastically reduce the computational effort required for the MD simulations, allowing us to explore longer transport timescales as well as reduced errors through repeated measurements. Furthermore, the reduced computational cost allows us to freely explore different molecular dynamics parameters.

Machine learned force fields are generated within the implementation of the VASP code. As such, the calculations are based on *ab initio* MD data and first a sufficient amount of such reference data has to be gathered, sampling the desired phase space for the later ML-FF exploitation. Any processes not captured during the training procedure can thus not be adequately contained in the force field. As such, in order to capture sufficient phase space, we trained in a temperature range from 500 K to 1000 K, using a temperature ramp of the used Langevin thermostat with friction coefficients 5ps<sup>-1</sup> for all elements and the lattice with a virtual mass of 1000 amu and under a pressure of 1 atm, simulated in the NpT ensemble. The BaZr<sub>0.75</sub>Y<sub>0.25</sub>O<sub>3</sub>H<sub>0.25</sub> bulk was modeled in 2x2x2 supercell containing 8 formular units with one hydrated oxygen vacancy. The total simulation time during the training was 100 ps, sampled by 100000 molecular dynamics steps of 1fs. For gathering the *ab initio* data, we employed a DFT setup of a Γ centered *k*-point grid of 2x2x2, 520 eV plane wave cutoff energy, an energy convergence criterium of 10<sup>-5</sup> eV and a gaussian smearing of electronic bands of 0.02eV. The mass of the hydrogen atoms was artificially set to 4 amu, which reduces the required periodicity of the MD sampling, allowing for a 1fs time step and therefore reduces the computational effort correspondingly. This inevitably introduces deviations as compared to experimental data due to the introduced isotope effect [28]. However, we can expect that even a non-classical isotope effect for hydrogen is independent of temperature. As such, the self-diffusivities and conductivities we calculate at a given simulation temperature deviate by an unknown factor of the isotope effect. However,





the activation energy for the transport can be assumed to be independent of the hydrogen mass.

After training, the AIMD data was used to generate a ML-FF with a two-body and three body descriptor range of 6Å and 4Å, respectively. The total number of resulting basis sets are 591, 590, 769, 8816 and 6218 for Ba, Zr, Y, O, and H atoms, respectively. This process is quite memory intensive for the employed number of descriptors, such that a total of 3TB of RAM was necessary to successfully generate the force field.

In order to obtain ionic trajectories, which give statistically significant information about self-diffusivity properties, those trajectories have to be obtained from the microcanonical ensemble, also called the *NVE* ensemble. Here the *N* stands for the particle number, *V* for the volume and *E* for the total energy of the system, all of which have to be conserved. To allow for such a measurement in the *NVE* ensemble, we first have to equilibrate the lattice at a given target temperature to obtain the volume through the *NpT* ensemble, where pressure and temperature are controlled through a suitable barostat and thermostat, respectively. From that resulting volume, we perform a further calculation in the *NVT* regime, using a thermostat to supply us an ionic configuration with the desired temperature, again after equilibration. With the ionic configuration obtained from this procedure, we can then start the measurement in the *NVE* ensemble. For our calculations, we used the same thermostat parameters as described for the training scheme, previously. From the resulting equilibrated configurations of the *NpT* regime, we can estimate the thermal expansion of our studied material. The resulting data as compared to experimental work of Han et al. [29] is illustrated in Figure 8. We find a value of  $(1.7 \pm 0.5) \times 10^{-5} \text{K}^{-1}$  which is in reasonable agreement with the experimental reference data.



Figure 19: Experimental lattice constant over temperature and thermal expansion for BaZr<sub>0.75</sub>Y<sub>0.25</sub>O<sub>3-6</sub> from reference [25] (left) and equilibrated *NpT* ML-FF molecular dynamics simulation of the hydrated material, with  $\sigma$  gaussian error interval from all equilibrated time steps (right). The grey data points are excluded from the fit, since they are outside the targeted temperature range for which adequate phase space sampling

To measure the self-diffusivity properties of the H<sup>+</sup> in the system, we performed MD simulations in the *NVE* ensemble with a total simulation time of at least 500ps, approaching the ns scale. This simulation time corresponds to how many steps can be achieved within one day with a 0.5fs time step on one node of the used supercomputer JURECA at JSC. Longer simulation times are possible, and corresponding calculations will be performed in the near future. The resulting average mean square displacements of the H<sup>+</sup> from their starting positions is shown in the left panel of Figure 9. Using vaspkit [30], we fitted the MSD curve to obtain the self-diffusivity *D* as a function of temperature *T*.





#### With the formula

$$\sigma = \frac{N \cdot q \cdot D(T)}{V \cdot k_B \cdot T}$$

for  $\sigma$  is the conductivity, where N is the number of particles per volume V, q is the charge of the particle and  $k_B$  is the Boltzmann constant, we can then calculate the conductivities for each temperature. The results are depicted in the right panel of Figure 9 together with an Arrhenius fit to the curve of the form

(1)

$$k = A \cdot \exp\left(\frac{-E_a}{k_{\rm B}T}\right),\tag{2}$$

with some pre-factor A and exponent containing  $E_a$ , the activation energy over the thermal energy  $k_BT$ , which can be determined from the slope of the fit in the right panel of Figure 9. This procedure results in an estimated activation energy of  $0.13\pm0.05$  eV as compared to reported values for BZY20 of  $0.46\pm0.01$  eV [31] from experiments and 0.32eV from kinetic MC simulations [24]. Our results are therefore not in agreement with the references, but are within the same order of magnitude. However, we expect that by sampling the conductivities over more data as described by [32] and further data analysis of the trajectories, we will find more conclusive results. The fit error of 0.05eV likely vastly underestimates the total error of our current analysis, since due to the stochastic nature of the molecular dynamics simulations, there is significant error on the temperature, volume and total energy. Through repeated measurements, the corresponding stochastic error can be reduced and estimated. For example, if we would treat the data points for 800K and 500K in the right panel of Figure 9 as outliers and determined  $E_a$  solely from the 600K and 700K data points, we would obtain a value for the energy barrier of 0.3eV.



Figure 22: Average mean square displacement (MSD) of  $H^+$  in hydrated BaZr<sub>0.75</sub>Y<sub>0.25</sub>O<sub>3-6</sub> at varying temperature (left) and Arrhenius plot of resulting conductivities as a function of inverse temperature (right).





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In the next steps, we will extend our studies to longer simulation times, perform more MD simulations to gather more exploitable MSD data. Additionally, we can extract information about the ionic vibrations from the trajectories, allowing us insights into the density of vibrational states which can be compared to experimental Raman and IR spectra. If possible, we aim to extend our model to larger unit cells, which could also reduce noise of the MD trajectories and include oxygen ion and co-ionic transport within the ML-FF. This would also enable us to perform a detailed study on the role of the Coulomb configuration of the dopant atoms on transport properties.





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#### 3. Conclusions

The ECOLEFINS project offers an innovative way to produce green olefins. Our DFT-based computer assisted material design can provide valuable insights into possible new co-ionic electrolyte materials. In close collaboration with our project partners, we have explored the potential for co-ionic conductivity in perovskite materials and found promising candidates for co-ionic electrolytes. In preparation for our further steps for the simulation of co-ionic transport, we have explored new methods employing machine learned force fields, which we aim to exploit in the second half of the project period. Beyond this, we have modeled grain boundaries of Y/Yb-doped Barium Zirconate, showing significant driving force for the segregation of dopants to the grain boundaries. Experimental results from our partners show that this segregation also directly improves the grain boundary conductivity. Our future work will focus on the study of co-ionic transport in prototype and novel electrolyte materials and defect chemistry of reference. This work might contribute to the development of the co-electrolysis reactor within the ECOLEFINS project, and, in the broader sense, to reducing carbon emissions and more ecological pathway for light olefin production.





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