

## THE MECHANISM OF PROTON DIFFUSION IN ABO<sub>3</sub> PEROVSKITE OXIDES

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### EXECUTIVE SUMMARY

Perovskite oxides (ABO<sub>3</sub>) are well-known proton conductors. However, the role of the A-site ion on proton diffusion in perovskite oxides is not clear. By performing detailed density functional theory (DFT) calculations, the PI investigated the effect of A ion vacancy on proton transfer in yttrium-doped BaZrO<sub>3</sub>, which is one of the widely studied perovskite oxides.

The study showed that the presence of A ions reduces the barrier for proton diffusion in a perovskite oxide, demonstrating the significance of perovskite structures as proton conductors. This also showed that proton movement in a perovskite oxide is governed by hydroxide ion rotation and proton transfer from one oxygen to another. Both these motions are strongly coupled to lattice deformations. The PI identified the key physical mechanisms and the energy barriers associated with both hydroxide ion rotation and proton transfer by performing nudged elastic band (NEB) calculations. Finally, the PI calculated the bond strength and showed that the presence of an A ion can reduce the bond strength between O and B ions, thereby reducing the energy barrier for local lattice deformations.

### RESEARCH CHALLENGE

Although the proton transport mechanisms in perovskite oxides have been explored [1–5], the mechanisms governing the lower activation energy of proton diffusion in perovskite oxides remain unclear. Therefore, the design and development of novel proton-conducting solid oxide electrolytes with high conductivity remain a significant challenge. In addition, another key question that has not been addressed regarding proton transport in perovskite oxides is the role of A-site ions on proton diffusion; *i.e.*, why do good proton conductors have the ABO<sub>3</sub> perovskite structure instead of, for example, the BO<sub>3</sub> structure with BO<sub>6</sub>-octahedrons?

Clear insights may be obtained by analyzing the role of A-site ions on the proton diffusion mechanism by considering the elementary steps underlying the proton transfer, hydroxide ion rotation, and the coupling of lattice dynamics to hydroxide ion rotation, which does not have a negligible barrier as shown in [6]. In this work, the investigator performed DFT calculations to address the two key questions above. This is the first systematic study on the origin of activation energy of proton transfer and hydroxide ion rotation, and the role of A-site ions, providing a deep understanding of the advantage of perovskite oxide as a proton conductor.

### METHODS & CODES

All DFT calculations were performed using the Vienna Ab initio Simulation Package [7–9]. The Perdew–Burke–Ernzerhof [10] exchange–correlation functional was employed based on the projector augmented-wave method [9]. The cutoff energy for the plane-wave basis set was 500 eV for all calculations, which were nonspin polarized. The migration energy barriers were calculated using the climbing-image nudged elastic band method [11].

### RESULTS & IMPACT

Based on DFT calculations, the origin of the activation energy of proton transfer and hydroxide ion rotation were revealed. Specifically, the outward O–B–O bending and A ion motions and hydroxide ion reorientation govern the hydroxide ion rotation process while the inward O–B–O bending motion and donor oxygen–proton–acceptor oxygen interactions govern the proton transfer process. The presence of A ions reduces the bond strength between O and B ions, thereby reducing the energy barrier for local lattice deformations such as the O–B–O bending motion. In addition, the presence of A ions decreases the bonding strength of protons with donor oxygen and increases the bonding strength of protons with acceptor oxygen, promoting proton motion from donor oxygen to acceptor oxygen. This work provides a thorough atomistic understanding of the role of A-site ions on proton diffusion in perovskite oxides and the results can enable design and discovery of novel materials with improved proton diffusion properties.

### WHY BLUE WATERS

This project required large-scale *ab initio* simulations to obtain the origin of activation energy of proton diffusion in solid oxides. For the DFT calculations, using eight to 10 nodes (256 to 320 cores) for each job can achieve the best performance, which is attributed to the power of Blue Waters and the support of project staff. Thus, running *ab initio* simulations on Blue Waters was easy and quick, speeding up the research greatly.

### PUBLICATIONS & DATA SETS

Y. Jing and N. R. Aluru, “The role of A-site ion on proton diffusion in perovskite oxides (ABO<sub>3</sub>),” *J. Power Sources*, vol. 445, p. 227327, Jan. 2020.

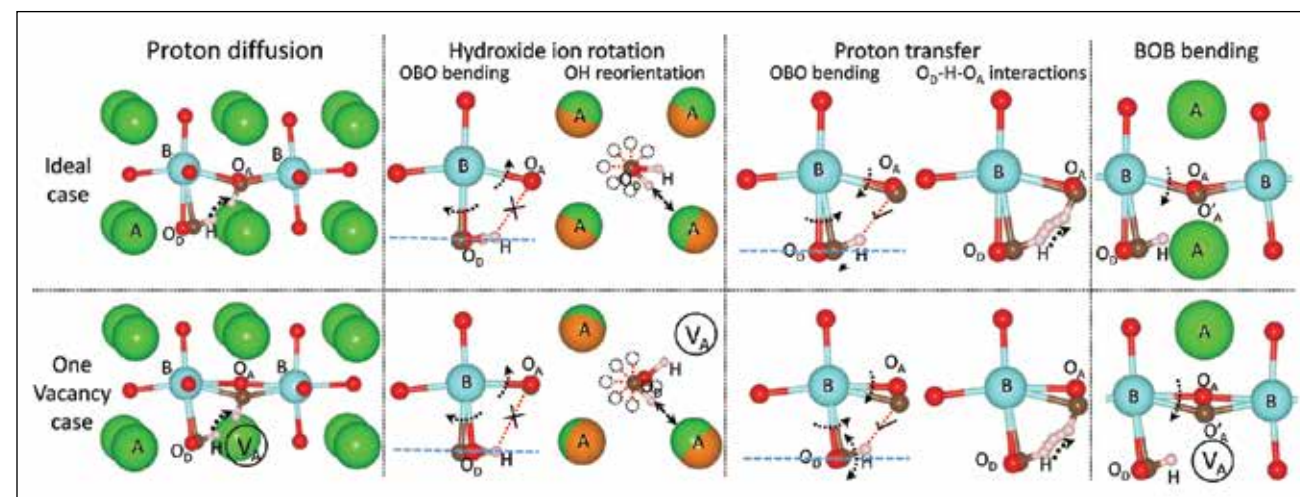


Figure 1: Schematic illustration of the proton diffusion mechanism in an ABO<sub>3</sub> perovskite oxide without (top row) and with (bottom row) one A ion vacancy.