

RESEARCH ARTICLE

Strain-induced tunable energy barrier of proton diffusion in Y-doped BaCeO₃ and Y-doped BaZrO₃Hongwei Niu¹  | Yuhang Jing^{1,2} | Yi Sun¹ | Licheng Guo¹ | Narayana R. Aluru^{2,3} | Weiqi Li⁴ | Jianqun Yang⁵ | Xingji Li⁵¹Department of Astronautical Science and Mechanics, Harbin Institute of Technology, Harbin, China²Beckman Institute for Advanced Science and Technology, National Center for Supercomputing Applications (NCSA), University of Illinois at Urbana-Champaign, Urbana, Illinois, USA³Walker Department of Mechanical Engineering, Oden Institute for Computational Engineering and Sciences, The University of Texas at Austin, Austin, Texas, USA⁴School of Physics, Harbin Institute of Technology, Harbin, China⁵Technology Innovation Center of Materials and Devices at Extreme Environment, Harbin Institute of Technology, Harbin, China

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Funding information

International Postdoctoral Exchange Fellowship Program of China, Grant/Award Number: 20140016; National Centre for Supercomputing Applications; National Natural Science Foundation of China, Grant/Award Numbers: 12172112, 11932005, 11974091; National Science Foundation, Grant/Award Number: 1545907

Summary

In this paper, the strain effects on the energy barrier of proton diffusion in Y-doped BaCeO₃ (BCY) and Y-doped BaZrO₃ (BZY) are investigated by detailed density functional theory calculations. The energy barrier of proton rotation decreases when the tensile strain is applied. For intra-octahedral proton transfer, the energy barrier decreases when the tensile strain is applied while for inter-octahedral proton transfer the energy barrier increases when the tensile strain is applied. However, we found that for intra-octahedral proton transfer the energy barrier of BZY shows the opposite strain effect. To understand the underlying mechanism behind this opposite trend we decomposed proton diffusion into three elementary steps and the opposite trend of the energy barrier of BCY and BZY during intra-octahedral proton transfer is pinpointed to the opposite bond order change of the hydrogen bond. In all, we explored the strain effects on the energy barrier of proton diffusion in BCY and BZY from a microscopic perspective, showing the potential to tune the energy barrier of proton transport in perovskite oxide with strain engineering and thus design novel proton conductors.

KEYWORDS

density functional theory, energy barrier, perovskite oxide, proton diffusion, strain effect

1 | INTRODUCTION

Renewable intermittent energy like wind and solar resources is not constantly available and predictable. Therefore, battery technologies are currently getting

attention to store them for later use. Proton-conducting solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOECs) technologies are highly promising for efficient conversion of chemical energy of hydrogen into electricity and vice versa without forming any air

pollutants.^{1–3} Since the beginning of proton-conducting SOFC/SOEC development, many acceptor-doped perovskite oxides have been used for its components.^{4–7} In particular, these with noticeable proton conductivity and reasonable chemical and mechanical stability are excellent candidates for electrolytes of both SOFCs and SOECs.^{8–11} Discovering material with high proton conductivity and understanding the mechanism behind proton transport remains important goal for the proton-conducting research community.

Proton cannot exist freely in perovskite oxide due to its extremely high charge density. It always resides on a host oxide ion to neutralize the charge density. In typical perovskite oxides with a chemical formula of ABO_3 , proton either rotates around its host oxide ion or migrates between different host oxide ions.^{9,12} When it transfers between two neighboring oxide ions belonging to the same BO_6 octahedron, the process is called intra-octahedral proton transfer while it transfers between two oxide ions belonging to two neighboring BO_6 octahedrons, the process is called inter-octahedral proton transfer. The proton conductivity can be described as¹³:

$$\sigma_{\text{proton}} = \frac{\sigma_0}{T} e^{-E_A/k_B T}, \quad (1)$$

where E_A is the activation energy of proton diffusion (rotation and transfer). Both the rotation and transfer processes lead to the proton diffusivity in perovskite oxide and the low energy barrier of proton rotation and transfer largely contributes to high proton conductivity in perovskite oxide.

Strain engineering is a potential route for ion-conducting tuning.^{14–16} Research interest arose on the strain effect of proton conductivity^{17–21} since the low energy barrier of proton conductors allows good ionic conductivity at reduced operating temperatures.²² Among all the proton-conducting acceptor-doped perovskite oxides investigated, Y-doped BaCeO_3 (BCY) and Y-doped BaZrO_3 (BZY) manifest excellent proton conductivity.^{22–25}

However, there are considerable discrepancies in the strain effect of BCY and BZY between experiments and simulations. Larger E_A (smaller σ_{proton}) is observed in both BCY and BZY in experiments when compressive isotropic pressure is applied,^{17–19} while a simulational work on BZY forecast the opposite trend.²⁰ Enhanced proton conductivity in BZY is discovered in the experiment when tensile biaxial stress is applied and it is supported by a first principle molecular dynamic simulation work,²¹ but it is in conflict with a reactive molecular dynamic simulation work predicting maximum conductivity under an optimal compressive strain.²⁰ The variance between experiments and simulations may attribute

to the lack of accuracy of simulation models. However, it should also be noted that the experimental data are very limited and the strain effect varies with the synthesis method. To the best of our knowledge, very few studies extend the investigation of the strain effect to BCY and BZY.

In the present work, we focus on the strain effect on the activation energy of proton diffusion in BCY and BZY. We first calculate the energy barrier of proton diffusion for BCY and BZY under strain, and then by studying the transition states in the transition path, we propose the elementary steps underlying proton diffusion to obtain microscopic insight on the proton diffusion, as is previously used in References 26. Finally, based on the elementary steps, we analyze the reasons behind the strain effect on the activation energy of proton diffusion in BCY and BZY.

2 | COMPUTATIONAL DETAILS

The density functional theory (DFT) calculations are performed with the Vienna Ab initio simulation package^{27–29} using the projector augmented wave method.²⁹ The Perdew–Burke–Ernzerhof³⁰ exchange–correlation functional is utilized and the cutoff energy for the plane-wave basis set is set to 500 eV. In geometry optimization, all atoms are relaxed using the conjugate gradient method until the forces on each atom are less than 0.02 eV/Å. The climbing image nudged elastic band (CI-NEB) method³¹ is used to find the minimum energy path connecting the initial and final configuration of proton rotation and transfer. The energy barrier along the path is thus derived. The bond order between atoms is computed by density-derived electrostatic and chemical (DDEC6) technique.³²

The unit cell of BaCeO_3 and BaZrO_3 are optimized using a $6 \times 6 \times 6$ Monkhorst-Pack k-points mesh. The lattice constants of BaCeO_3 and BaZrO_3 are determined to be 6.250 and 4.223 Å, respectively, which are consistent with previous calculations.³³ Then, a $2 \times 2 \times 2$ supercell and $3 \times 3 \times 3$ supercells are constructed based on the optimized unit cell for BaCeO_3 and BaZrO_3 , respectively. Next, two B-site ions are substituted with two dopants ions. The preferred positions of the two dopants ions are chosen by locating the two dopants ions at different atomic sites and comparing the total energies of the system. The lattice constants of the optimized Y-doped BaCeO_3 and Y-doped BaZrO_3 are determined to be 6.246 and 4.238 Å, respectively. Finally, two protons are introduced to the supercell. Again, the preferred positions of the two protons are chosen by locating the two protons at different atomic sites and comparing the

total energies of the system. The lattice constants of the optimized hydrated BCY and BZY are determined to be 6.268 and 4.236 Å, respectively. The optimized hydrated BCY and BZY systems are shown in Figure 1A, B. In all calculations below, only one proton's motion is taken into account while the second proton is bonded to the initial oxygen and relaxed freely.

3 | RESULTS

3.1 | Energy barrier of proton rotation and transfer under strain

The energy barriers of proton rotation and transfer are calculated for both BCY and BZY under a tensile or compressive strain up to $\pm 6\%$ with the CI-NEB method, as shown in Figure 2. The energy barrier of proton rotation and transfer of BZY under strain are compared with a previous DFT work²¹ of undoped BaZrO₃ for verification in Table 1. From Table 1, the two works show the same descending trend for the energy barrier of proton rotation and the same increasing trend for the energy barrier of proton transfer when strain is increased. The difference between the two works may attribute to the presence of Y dopants in our system. In Figure 2, for both BCY and BZY, the energy barrier of proton rotation decreases when the tensile strain is applied. The trend of the energy barrier of intra-octahedral proton transfer is rather

different for BCY and BZY. For BCY the energy barrier decreases when the tensile strain is applied while for BZY the energy barrier increases. For the inter-octahedral proton transfer energy barrier of BCY, it increases when the tensile strain is applied. That for BZY is unlikely to happen due to the local structure as shown in Figure 1D. For BCY, the proton is close to both intra- and inter-octahedral oxygen (see Figure 1C) while for BZY the proton is only close to intra-octahedral oxygen (see Figure 1D). From Figure 2, we can also find all three energy barrier curves of BCY are not monotonous and take local minima when strain equals to zero. This is attributed to the local structure of BCY that the proton is close to inter-octahedral oxygen (see Figure 1C). When strain is applied, the distance between the proton and inter-octahedral oxygen is altered. Therefore, for either proton rotation, intra-octahedral proton transfer or inter-octahedral proton transfer, the inter-octahedral oxygen reorients due to the hydrogen bond interaction. Therefore, the energy barrier is enlarged. However, when the strain equals to zero, the inter-octahedral oxygen is stable and does not reorientate. For BZY the proton is not close to inter-octahedral oxygen, therefore the inter-octahedral oxygen does not reorientate as the strain is applied due to the lack of hydrogen bond interaction. Thus, the local minima are not observed in the energy barrier curves of BZY.

To understand the reasons behind the same or opposite trends of the strain effect for BCY and BZY we

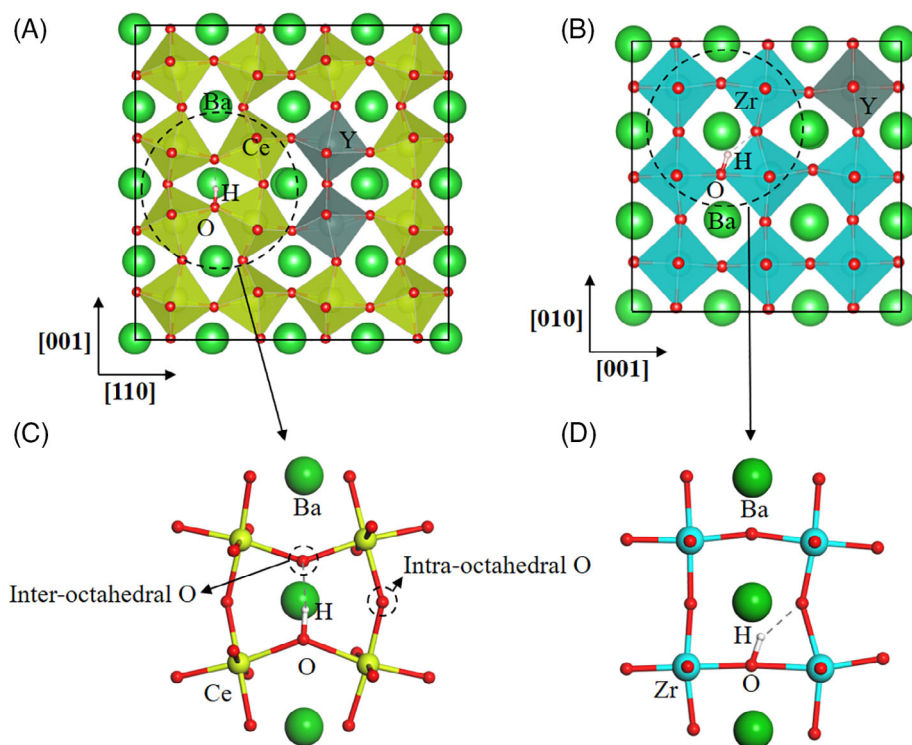


FIGURE 1 Optimized hydrated (A) BCY and (B) BZY systems and the local structures of (C) BCY and (D) BZY within the systems

FIGURE 2 Energy barrier of proton rotation and transfer for BCY and BZY under strain

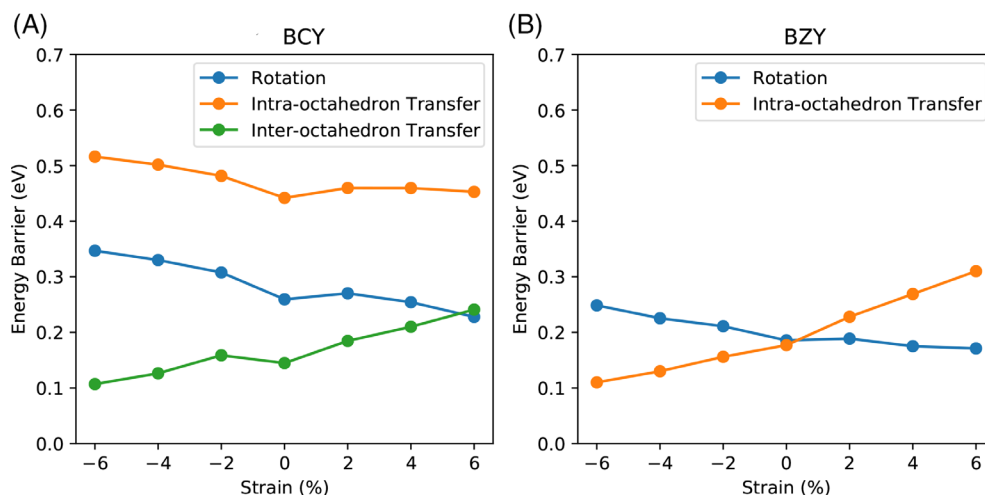


TABLE 1 Comparison of one previous DFT work²¹ of undoped BaZrO₃ with our DFT results of BZY

Strain	−6%	−5%	−4%	−2%	0	2%	4%	5%	6%
Proton rotation									
Reference 21		0.539		0.339	0.246	0.185		0.172	
This work	0.249		0.225	0.211	0.186	0.189	0.175		0.171
Proton transfer									
Reference 21				0.009	0.038	0.093		0.314	
This work	0.110		0.130	0.156	0.177	0.228	0.269		0.310

further decompose proton diffusion into elementary steps and investigate the strain effect on each elementary step. Details of the decomposition and the strain effect on the elementary steps are discussed Sections 3.2 and 3.3, respectively.

3.2 | Elementary steps underlying the proton rotation and transfer

To understand the mechanism of proton rotation and transfer, we investigated the initial and saddle configurations (the configuration with maximum energy barrier) in the NEB calculations and proposed the elementary steps underlying proton rotation and transfer. In our previous work, we have shown the elementary steps for BZY²⁶ and in this work, we focused on the elementary steps for BCY. The elementary steps for proton rotation and transfer do not change under a tensile or compressive strain up to $\pm 6\%$ based on our calculations and the cases with no strain are used as example to explain the detailed elementary steps.

First, we characterized three elementary steps of proton rotation of BCY: (a) outward O-B-O bending. The hydrogen bond H—O₂ is therefore weakened and the

proton is allowed to rotate in the OA plane, (b) proton rotation in the OA plane. The proton rotates out of the original OB plane toward the new OB plane, and (c) lattice relaxation. The proton reorients in the new OB plane and the system evolves to a lower energy state. The relative energy of these three elementary steps is plotted in Figure 3A–C. Figure 3A displays the relative energy against the O-B-O angle (see $\angle O_1BO_2$ of inset of Figure 3A). The energy barrier of this elementary step is 0.219 eV. Figure 3B shows the relative energy of proton rotation in the OA plane. The relative energy increases and arrives at the maximum when the proton is in the middle of O₁ and A ion (see the inset of Figure 3B), and then decreases as the proton ion further rotates to a new favorable orientation. The energy barrier of this elementary step is 0.042 eV. Figure 3C reveals the relative energy against the O-B-O angle (see $\angle O_1BO_2$ of inset of Figure 3C) during lattice relaxation. No energy barrier is associated with the lattice relaxation process. The system gradually evolves to a lower energy state as the O-B-O angle recovers. A new hydrogen bond H—O₃ is then formed in the new OB plane. The summation of the energy barriers of the first two elementary steps is 0.261 eV, which matches well with the NEB calculation of 0.259 eV. This suggests that our way decompose the

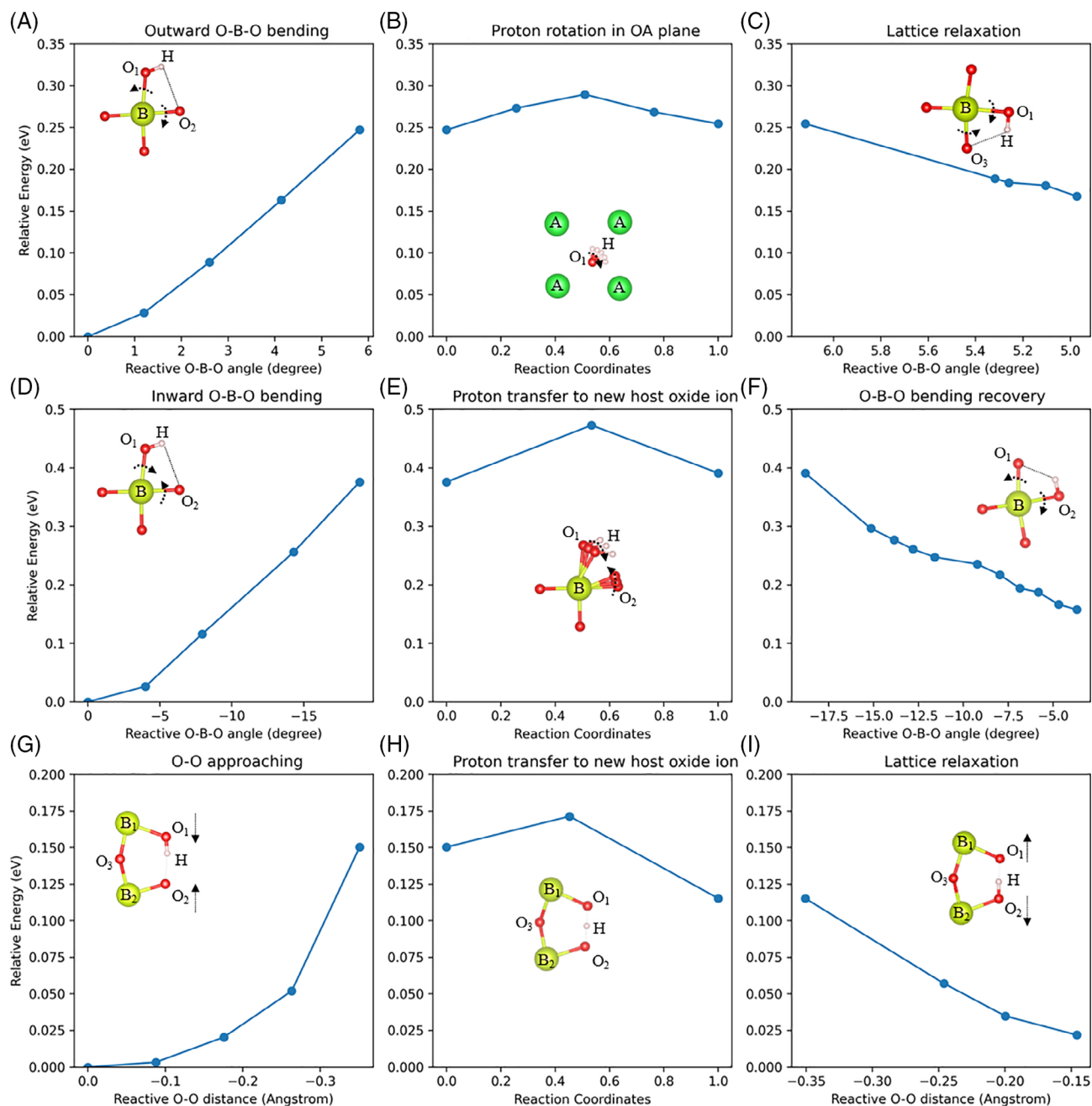


FIGURE 3 Energy barrier of elementary steps during proton rotation and transfer for BCY

total energy barrier provides insights into the proton rotation in BCY.

Second, the elementary steps underlying intra-octahedral proton transfer are proposed: (a) inward O-B-O bending. The distance between proton and O_2 is therefore decreased and the attraction between the proton and O_2 is increased, (b) proton transfer to a new host oxide ion, and (c) recovery of O-B-O bending. Figure 3D-F plotted the relative energy of the three elementary steps. Figure 3D displays the relative energy against the O-B-O angle (see $\angle O_1BO_2$ of inset of

Figure 3D) and the energy barrier of this elementary step is 0.349 eV. Figure 3E shows the relative energy of proton transfer to the new host oxide ion. The relative energy increases and arrives at the maximum as the proton is in the middle of O_1 and O_2 ion (see the inset of Figure 3E), and then decreases as the proton ion resides on O_2 . The energy barrier of this movement is 0.097 eV. Figure 3F shows the relative energy against the O-B-O angle (see $\angle O_1BO_2$ of inset of Figure 3F) during the recovery of O-B-O bending. The summation of the energy barriers of the first two elementary steps is

0.446 eV, which matches well with the NEB calculation of 0.442 eV.

Last, the elementary steps underlying inter-octahedral proton transfer are suggested: (a) O-O approaching. The distance between proton and O₂ is therefore decreased and the attraction between the proton and O₂ is increased, (b) proton transfer to a new host oxide ion, and (c) lattice relaxation. Figure 3G-I plotted the relative energy of the three elementary steps. Figure 3G displays the relative energy against the O-O distance (see O₁-O₂ of inset of Figure 3G) and the energy barrier of this elementary step is 0.130 eV. Figure 3H shows the relative energy of proton transfer to the new host oxide ion. The relative energy increases and arrives at the maximum as the proton is in the middle of O₁ and O₂ ion (see the inset of Figure 3H), and then decreases as the proton ion resides on O₂. The energy barrier of this elementary step is 0.021 eV. Figure 3I reveals the relative energy against the O-O distance (see O₁-O₂ of inset of Figure 3I) during the recovery of O-B-O bending. The summation of the energy barriers of the first two elementary steps is 0.151 eV, which matches well with the NEB calculation of 0.145 eV.

To confirm if the proton rotation and transfer of BCY are also composed of the proposed elementary steps

under strain, the decomposed energy barriers are also calculated for the cases under tensile or compressive strain. The summations of decomposed energy barriers under tensile or compressive strain are also consistent with NEB calculation as shown in Figure 4. Finally, to further understand the mechanism of the strain effect on the energy barrier, the strain effect on each elementary step is discussed in Section 3.3.

3.3 | Strain effect on the elementary steps

From Figure 4, we can see that the effect of strain on the barrier is mainly dominated by the effect of strain on the first elementary step. Thus, the effect of strain on the first elementary step is first studied.

For proton rotation of both BCY and BZY, the first elementary step is outward O-B-O bending. To study the strain effect on the energy barrier of this elementary step, the bond order between atoms is computed by the DDEC6 technique. We calculated the bond order changes of the hydrogen bond of initial and final configurations of the first elementary step, as shown in Table 2A. For BCY, hydrogen bond shows descending bond order

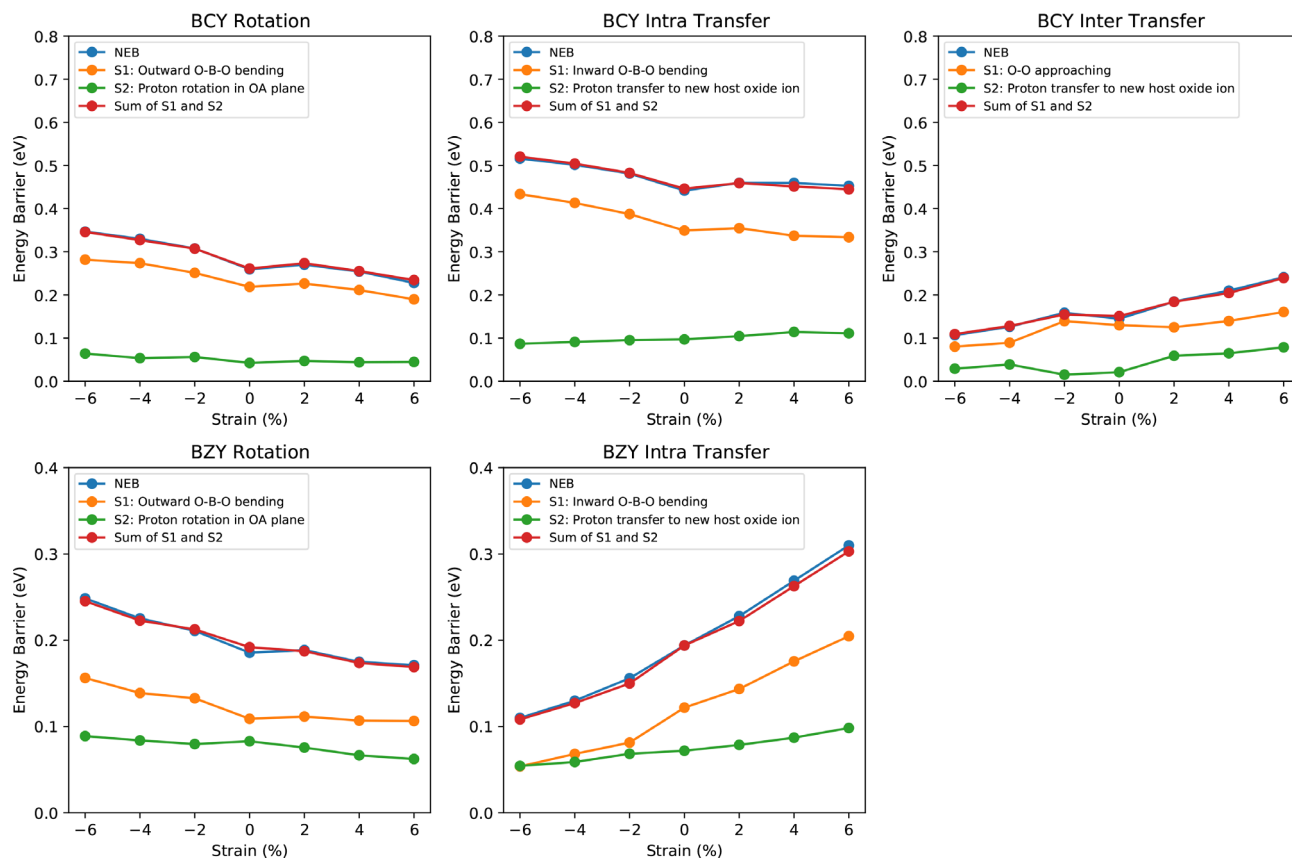


FIGURE 4 Energy barrier of proton rotation/transfer and their elementary steps for BCY and BZY under strain

change as tensile strain is applied, which corresponds to the decreasing energy barrier of the first elementary step as tensile strain is applied. For BZY, the hydrogen bond also shows descending bond order changes as tensile strain is applied. The energy barrier of the first elementary step of BZY also decreases as the tensile strain is applied and it shows the same mechanism as BCY.

For intra-octahedral proton transfer of both BCY and BZY, the first elementary step is inward O-B-O bending. We calculated the bond order changes of the hydrogen bond of initial and final configurations of the first elementary step, as shown in Table 2B. For BCY, as tensile

TABLE 2 Bond order changes and energy barriers BCY and BZY under strain during the first elementary step

(A) Proton rotation		
	$ \Delta_{\text{hydrogen bond}} $	Energy barrier (eV)
BCY (−6%)	0.16	0.28
BCY (+6%)	0.09↓	0.19↓
BZY (−6%)	0.05	0.16
BZY (+6%)	0.02↓	0.11↓
(B) Intra-octahedral proton transfer		
BCY (−6%)	0.16	0.43
BCY (+6%)	0.09↓	0.33↓
BZY (−6%)	0.08	0.05
BZY (+6%)	0.18↑	0.20↑
(C) Inter-octahedral proton transfer		
BCY (−6%)	0.13	0.08
BCY (+6%)	0.17↑	0.16↑

strain is applied, the bond order change of the hydrogen bond is decreasing, which corresponds to the decreasing energy barrier of the first elementary step. For BZY, however, hydrogen bond shows increasing bond order changes as tensile strain is applied, due to the different local structure as shown in Figure 1C,D. The energy barrier of the first elementary step of BZY increases as tensile strain is applied. Thus, for intra-octahedral proton transfer, the opposite trend of the energy barrier of the first elementary step of BCY and BZY is attributed to the opposite strain effect on the bond order change of the hydrogen bond.

Finally, for inter-octahedral proton transfer of BCY, the first elementary step is O-O approaching. We calculated the bond order changes of the hydrogen bond of initial and final configurations of the first elementary step, as shown in Table 2C. Hydrogen bond shows increasing bond order changes as tensile strain is applied, which corresponds to the increasing energy barrier of the first elementary step as tensile strain is applied.

From Figure 3, we can also observe that the energy barrier of the second elementary step has a limited strain effect. We further investigated the electronic density distribution (see Figure 5) during the intra-octahedral proton transfer of BCY as an example to confirm this observation. At the initial state (see the first row of Figure 5) of the second elementary step, both the hydroxide ion bond length and hydrogen bond length remain almost unchanged from −6% to 6% strain. At the saddle point (see the second row of Figure 5), the bond length of the hydroxide ion and the hydrogen bond is about equal and stay almost unchanged from −6% to 6% strain. We

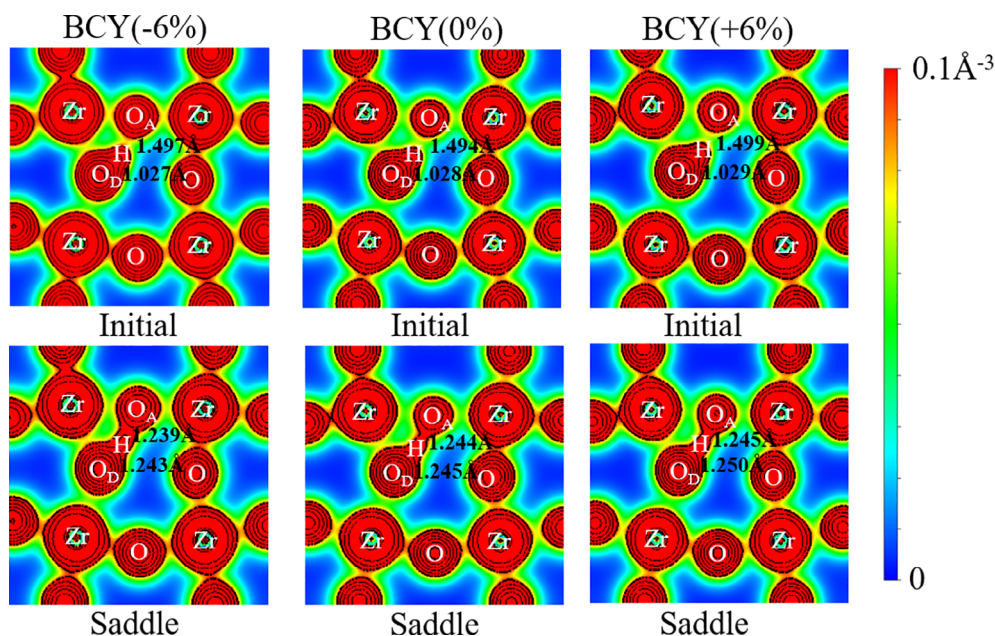


FIGURE 5 Electronic density distribution for BCY under strain during intra-octahedral proton transfer

therefore confirmed the second elementary step has a limited strain effect.

4 | CONCLUDING REMARKS

In this paper, the strain effect on proton diffusion in BCY and BZY is investigated using detailed DFT calculations. For both BCY and BZY, the energy barrier of proton rotation decreases when the tensile strain is applied. The trend of the energy barrier of intra-octahedral proton transfer is rather different for BCY and BZY. For BCY the energy barrier decreases when the tensile strain is applied while for BZY the energy barrier increases. For the inter-octahedral proton transfer energy barrier of BCY, it increases when the tensile strain is applied.

We proposed elementary steps underlying proton diffusion in BCY to provide an atomic-level understanding of the strain effect. For proton rotation in BCY, outward O-B-O bending weakens the hydrogen bond and then the proton is allowed to rotate in the OA plane. Hydrogen bond shows descending bond order changes as tensile strain is applied, which results in the decreasing energy barrier of the first elementary step as tensile strain is applied. For intra-octahedral proton transfer in BCY, inward O-B-O bending shortens the distance of the proton and new host oxide ion thus facilitating intra-octahedral proton transfer. For BCY, as tensile strain is applied, the bond order change of the hydrogen bond is decreasing. For BZY, hydrogen bond shows increasing bond order changes as tensile strain is applied and the energy barrier of the first elementary step increases as the tensile strain is applied. Therefore, for intra-octahedral proton transfer, the opposite trend of the energy barrier of the first elementary step of BCY and BZY is attributed to the different strain effects on the bond order change of the hydrogen bond. For inter-octahedral proton transfer in BCY, the distance between the old host oxide ion and the new host oxide ion is shortened, hence promoting inter-octahedral proton transfer. Hydrogen bond shows increasing bond order changes as tensile strain is applied, which corresponds to the increasing energy barrier of the first elementary step as tensile strain is applied. The current study provides a systematic understanding of the strain effect on proton diffusion in both BCY and BZY, showing the potential to tune the energy barrier with strain engineering.

ACKNOWLEDGEMENTS

This work is supported by the National Science Foundation under grant # 1545907, the National Center for Supercomputing Applications (NCSA), the NSF of China under Grant No. 12172112, 11932005, and 11974091, and

the International Postdoctoral Exchange Fellowship Program of China under Grant No. 20140016.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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How to cite this article: Niu H, Jing Y, Sun Y, et al. Strain-induced tunable energy barrier of proton diffusion in Y-doped BaCeO₃ and Y-doped BaZrO₃. *Int J Energy Res.* 2022;46(6):7816-7824. doi:10.1002/er.7682