Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Theoretical study on proton diffusivity in Y-doped $BaZrO_3$ with realistic dopant configurations

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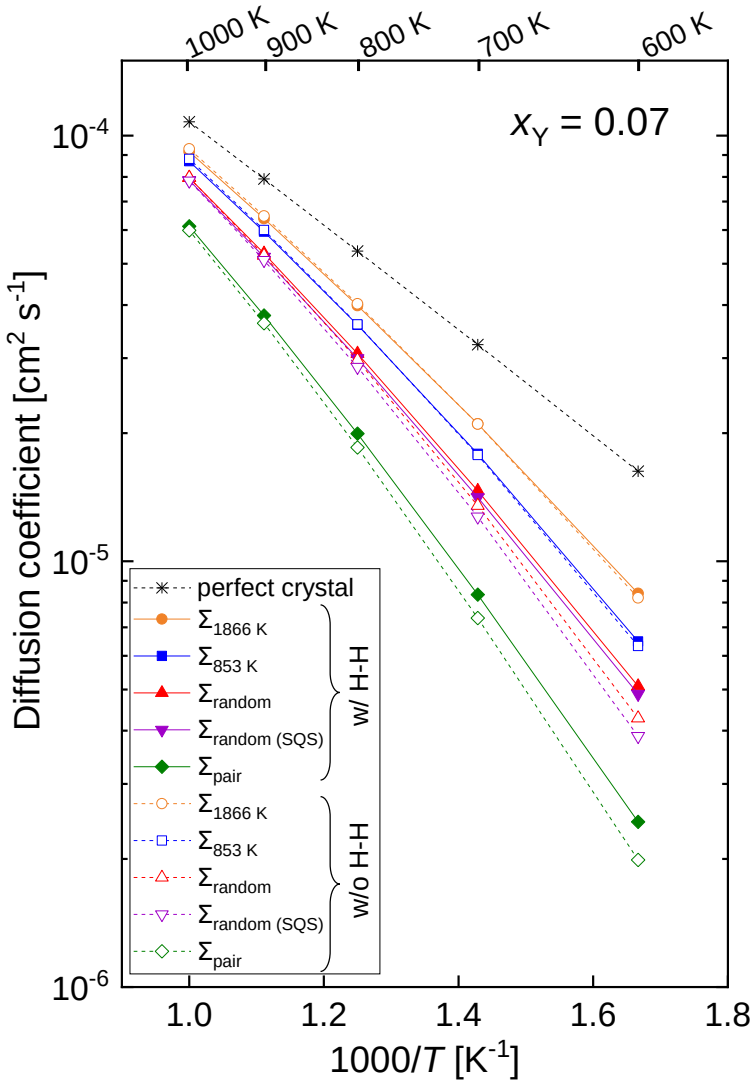

Figure S1. The calculated proton diffusion coefficients as a function of inverse temperature in various Y configurations at $x_Y = 0.07$. The solid and broken lines denote the proton diffusion coefficients with and without the H-H interaction. The purple lines show the proton diffusion coefficients in the SQSs corresponding to the random Y configuration (Σ_{random}). The black broken lines is the proton diffusion coefficients in the perfect crystal with neither H-H nor Y-H interaction.

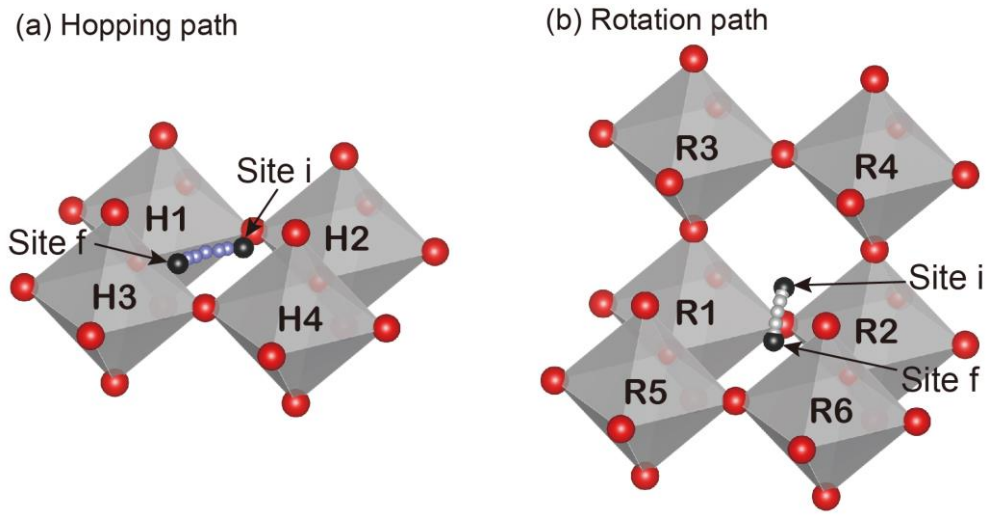

Figure S2. Adjacent Zr sites around the proton (a) hopping and (b) rotation paths, which were taken into consideration for Y local configuration [19]. Protons on sites i and f in the rotation path form an OH bond with the same O ion between R1 and R2. The site i is located on the plane through "R1, R2, R3, and R4", while the site f is on the plane through "R1, R2, R5, and R6". In the hopping path, sites i and f are located on the same plane as H1, H2, H3, and H4, forming an OH bond with the different O ions between "H1 and H2" and "H1 and H3", respectively.

Table S1. Calculated potential barriers of proton hopping with various configurations of Y dopants in Zr sites [19].

		Zr and Y configuration in B sites				$\Delta E_{i\to f}^{mig}$ / eV	$\Delta E_{f\to i}^{mig}$ / eV
# of Y	Path ID	H1	H2	H3	H4		
0	H0-1	Zr	Zr	Zr	Zr	0.25	0.25
1	H1-1	Y	Zr	Zr	Zr	0.21	0.21
	H1-2	Zr	Zr	Y	Zr	0.19	0.17
	H1-3	Zr	Zr	Zr	Y	0.42	0.42
2	H2-1	Y	Zr	Y	Zr	0.15	0.02
	H2-2	Y	Zr	Zr	Y	0.41	0.41
	H2-3	Zr	Zr	Y	Y	0.24	0.34
	H2-4	Zr	Y	Y	Zr	0.13	0.13
3	H3-1	Y	Zr	Y	Y	0.24	0.38
	H3-2	Y	Y	Y	Zr	0.05	0.05
	H3-3	Zr	Y	Y	Y	0.56	0.56
4	H4-1	Y	Y	Y	Y	0.45	0.45

Table S2. The calculated potential barriers of proton rotation with various configurations of Y dopants in Zr sites [19].

		Zr and Y configuration in B sites						$\Delta E_{\mathrm{i\to f}}^{\mathrm{mig}}$ / eV	$\Delta E_{\mathrm{f\to i}}^{\mathrm{mig}}$ / eV
# of Y	Path ID	R1	R2	R3	R4	R5	R6		
0	R0-1	Zr	Zr	Zr	Zr	Zr	Zr	0.17	0.17
1	R1-1	Y	Zr	Zr	Zr	Zr	Zr	0.18	0.18
	R1-2	Zr	Zr	Zr	Zr	Y	Zr	0.11	0.25
2	R2-1	Y	Y	Zr	Zr	Zr	Zr	0.25	0.25
	R2-2	Zr	Zr	Zr	Zr	Y	Y	0.09	0.31
	R2-3	Zr	Zr	Y	Zr	Y	Zr	0.20	0.20
	R2-4	Zr	Zr	Zr	Y	Y	Zr	0.17	0.17
	R2-5	Y	Zr	Zr	Zr	Y	Zr	0.08	0.29
	R2-6	Y	Zr	Zr	Zr	Zr	Y	0.11	0.22
3	R3-1	Zr	Zr	Y	Zr	Y	Y	0.20	0.32
	R3-2	Y	Zr	Y	Zr	Y	Zr	0.20	0.20
	R3-3	Y	Zr	Zr	Y	Zr	Y	0.20	0.20
	R3-4	Y	Zr	Zr	Zr	Y	Y	0.24	0.49
	R3-5	Y	Zr	Zr	Y	Y	Zr	0.08	0.37
	R3-6	Y	Y	Zr	Zr	Y	Zr	0.13	0.33
4	R4-1	Zr	Zr	Y	Y	Y	Y	0.17	0.17
	R4-2	Y	Y	Y	Y	Zr	Zr	0.21	0.11
	R4-3	Y	Y	Zr	Y	Zr	Y	0.40	0.40
	R4-4	Y	Y	Y	Zr	Zr	Y	0.30	0.30
	R4-5	Zr	Y	Y	Y	Zr	Y	0.48	0.34
	R4-6	Zr	Y	Y	Y	Y	Zr	0.45	0.22
5	R5-1	Zr	Y	Y	Y	Y	Y	0.17	0.17
	R5-2	Y	Y	Y	Y	Zr	Y	0.54	0.34
6	R6-1	Y	Y	Y	Y	Y	Y	1.08	1.08

Table S3. The pseudocode for estimating proton site energies in a given supercell of Y-doped $BaZrO_3$, which are estimated from the energy differences between adjacent sites depending only on the local Y configurations ($\Delta E_{i,j}$: site energy difference between sites i and j). However, the site energy is not uniquely determined due to slight inconsistency of $\Delta E_{i,j}$ between various local Y configurations, which is therefore estimated as the average value. n_{site} and n_{loop} denote the number of sites in the supercell and the number of loops, respectively. n_{loop} was here set to $n_{\mathrm{site}}/10$.

Algorithm: Site Energy Estimation ($\{\Delta E_{i,j}\}$, n_{site}, n_{loop})

Initialize:

Estimated site energy at site i in loop l: $E_i^{(l)} = \mathrm{nil}$ $(i = 1, 2, ..., n_{\mathrm{site}})$

for l **in** $1..n_{\mathrm{loop}}$ **do**

Initialize the set of unsampled sites: $S_{\mathrm{unsmp}} = \{1, 2, \ldots, n_{\mathrm{site}}\}$

Initialize the set of sampled sites: $S_{\mathrm{smp}} = \emptyset$

Randomly sample a starting point from S_{unsmp} (Starting site No.: i_0)

$E_{i_0}^{(l)} = 0$, $S_{\mathrm{smp}} \leftarrow S_{\mathrm{smp}} \cup \{i_0\}$, $S_{\mathrm{unsmp}} \leftarrow S_{\mathrm{unsmp}} \setminus \{i_0\}$

while $S_{\mathrm{unsmp}} \neq \emptyset$ **do**

Randomly sample an unsampled site adjacent to any sampled site

(Sampled site No.: i_{smp}, Adjacent site No.: i_{adj})

$E_{i_{\mathrm{smp}}}^{(l)} = E_{i_{\mathrm{adj}}}^{(l)} + \Delta E_{i_{\mathrm{adj}},i_{\mathrm{smp}}}$, $S_{\mathrm{smp}} \leftarrow S_{\mathrm{smp}} \cup \{i_{\mathrm{smp}}\}$, $S_{\mathrm{unsmp}} \leftarrow S_{\mathrm{unsmp}} \setminus \{i_{\mathrm{smp}}\}$

done

$E_{\max} = \max_i E_i^{(l)}$

for i **in** $1..n_{\mathrm{site}}$ **do**

$E_i^{(l)} = E_i^{(l)} - E_{\max}$

done

done

Output:

Averaged site energy at site i $(i = 1, 2, ..., n_{\mathrm{site}})$: $E_i^{\mathrm{ave}} = \frac{1}{n_{\mathrm{loop}}} \Sigma_l E_i^{(l)}$

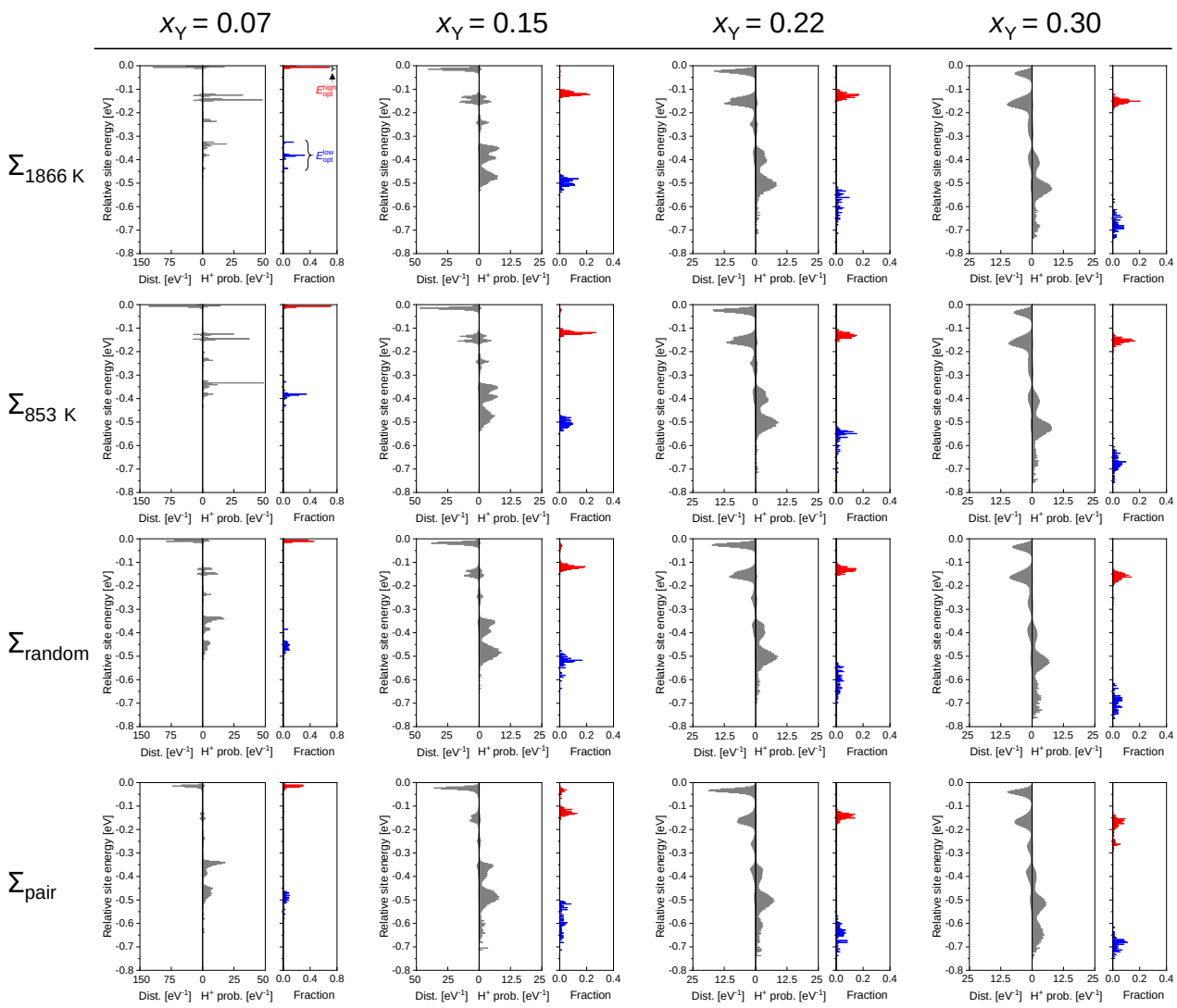

Figure S3. The normalized site-energy distributions (Dist.) in the 72 supercells at various Y concentrations and in various Y configurations (Σ_{1866K}, Σ_{853K}, Σ_{random}, and Σ_{pair}). The proton existence probability at 600 K (H^+ prob.) is also shown in each figure. The normalized histograms of the lowest and highest site energies along the optimal paths are shown on the right side by the blue and red bars, respectively.

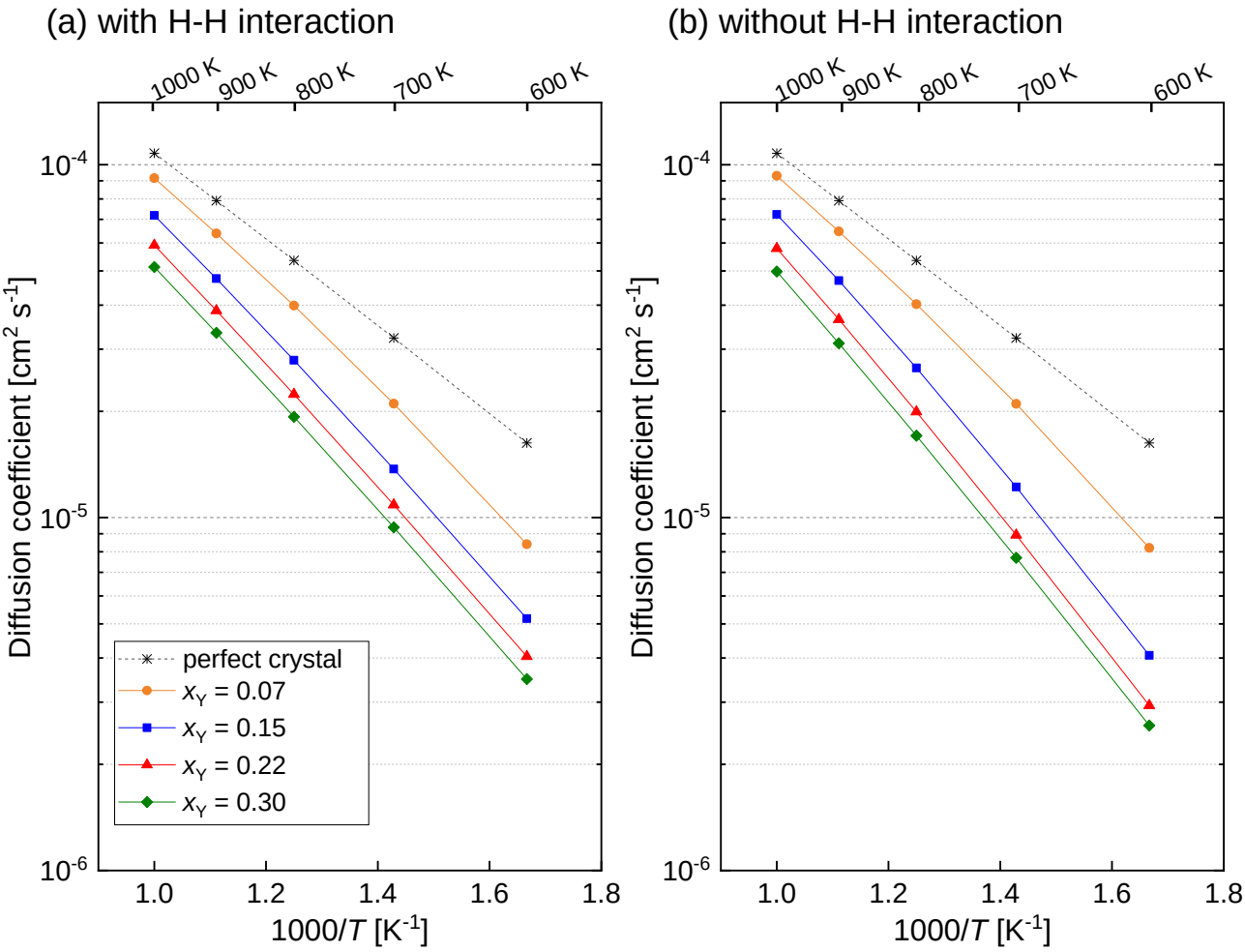

Figure S4. The calculated proton diffusion coefficients as a function of inverse temperature in the case of Σ_{1866K} configuration of Y dopants. Figures (a) and (b) show the proton diffusion coefficients with and without the proton-proton interactions, respectively. The site occupancies of Y dopants on the Zr sites, x_Y, are 0.07, 0.15, 0.22, and 0.3. The black broken lines show the proton diffusion coefficients in the perfect crystal with neither H-H nor Y-H interaction for reference.