

**Unraveling the role of La A-site substitution on oxygen ion diffusion
and oxygen catalysis in perovskite BaFeO₃ by data-mining
molecular dynamics and density functional theory**

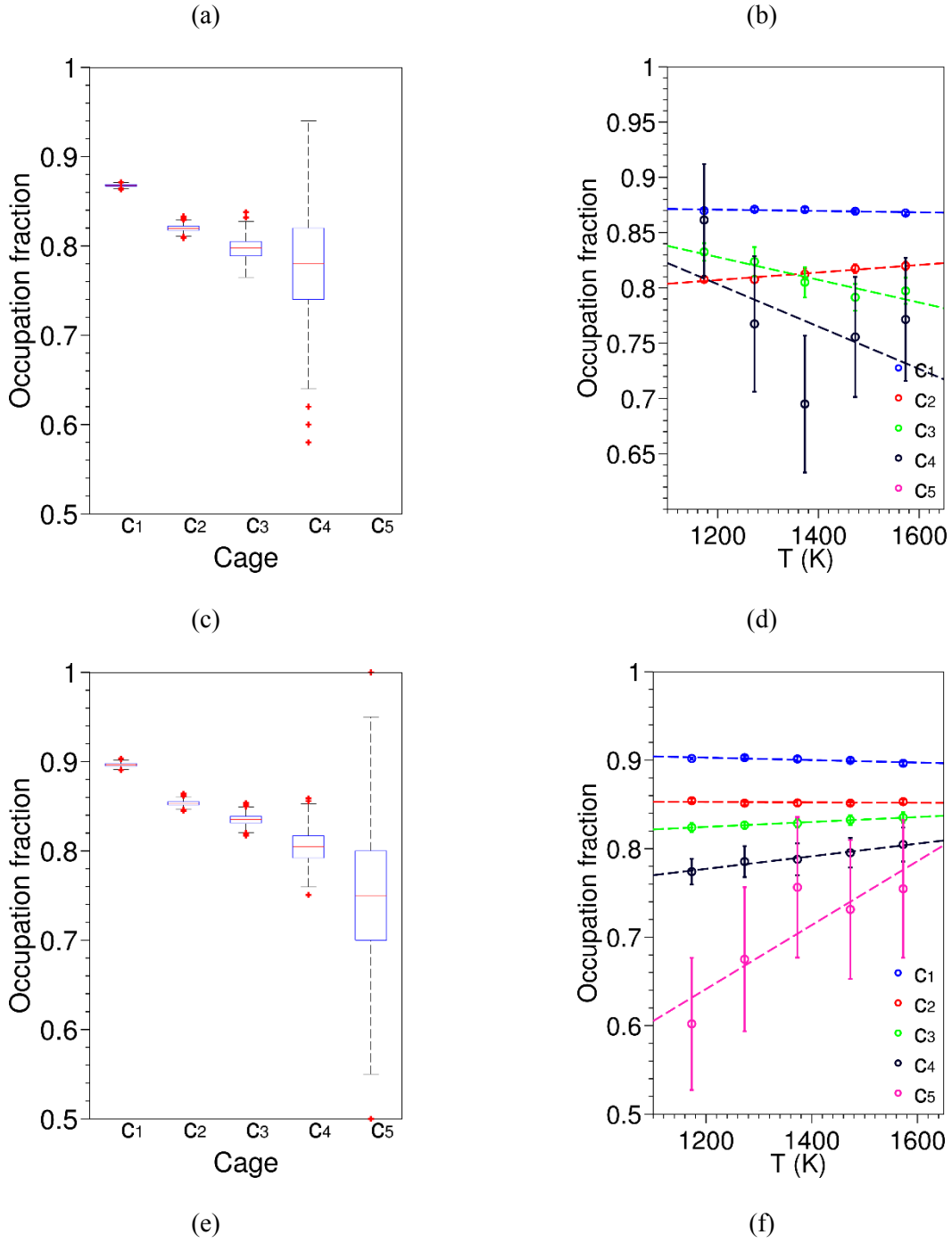
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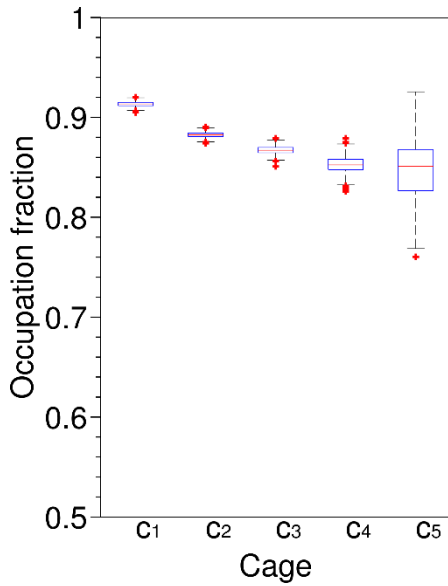
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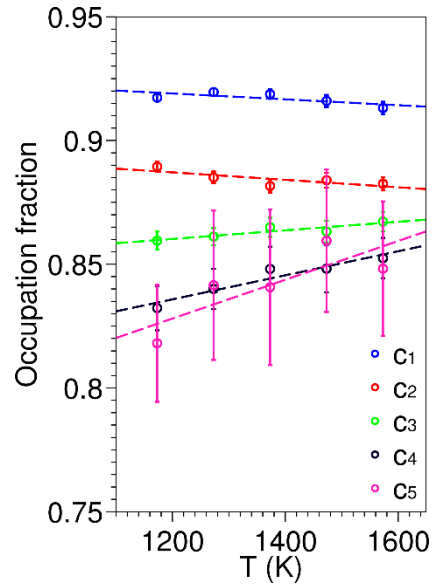
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Occupation fraction for different cages of $\text{Ba}_{1-x}\text{La}_x\text{FeO}_{3-\delta}$ ($x=0.1, 0.2, 0.3$ and 0.4)





(g)



(h)

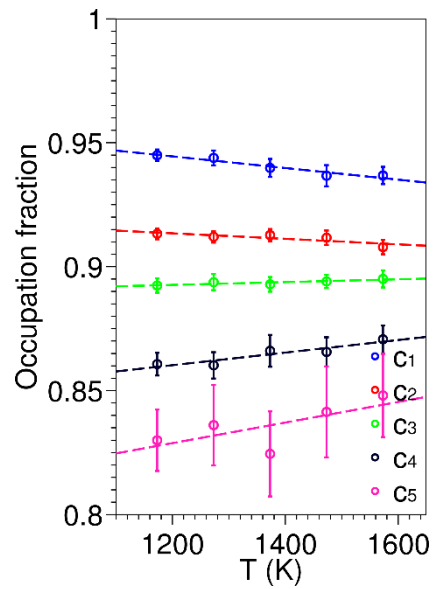
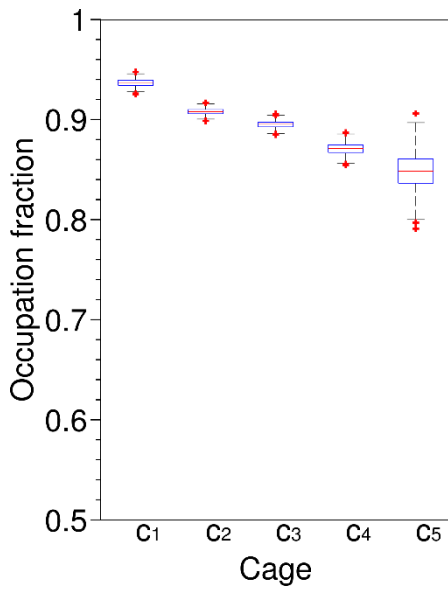
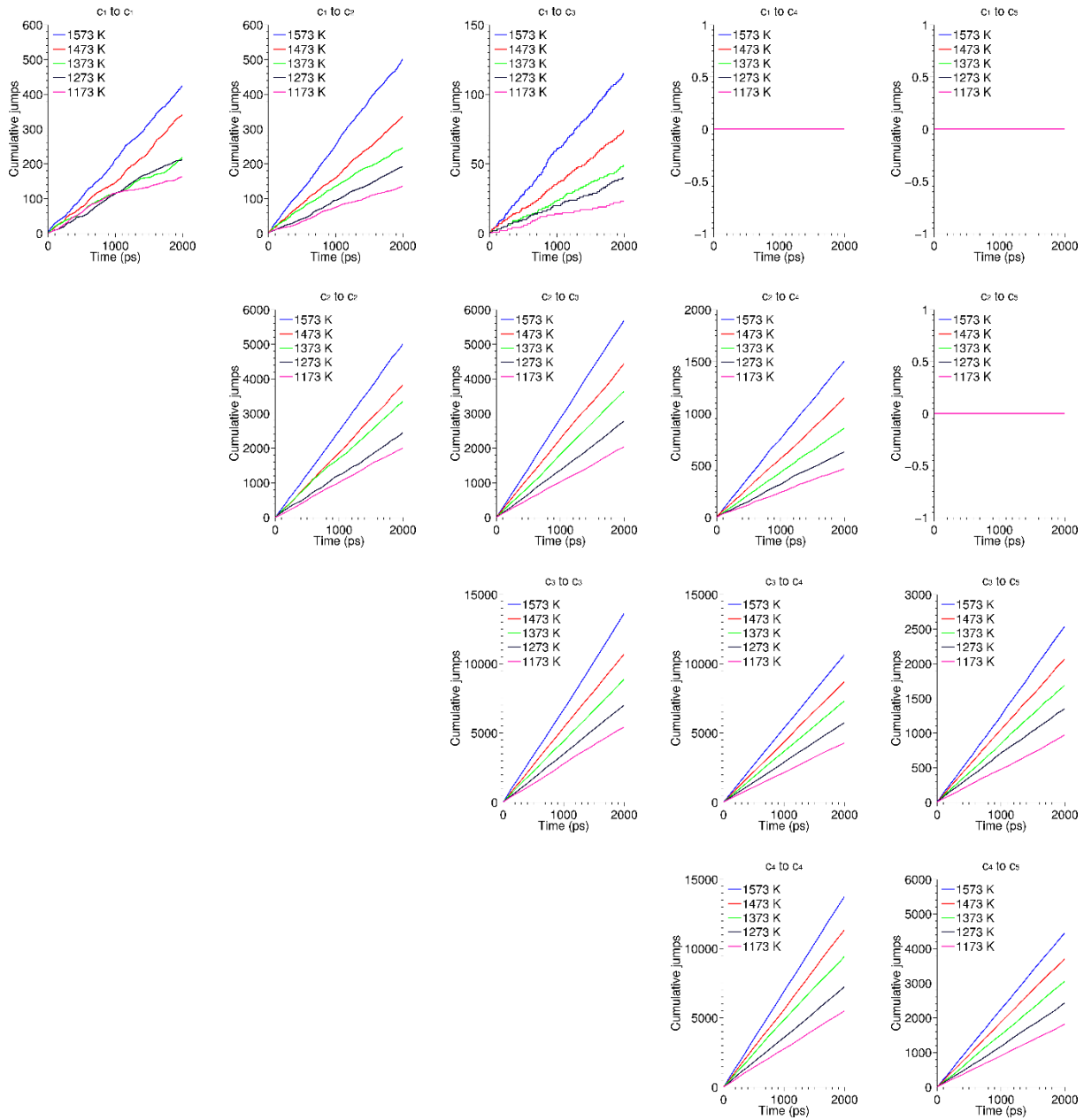


Figure S1. Occupation fractions of different cages at 1573 K of $\text{Ba}_{1-x}\text{La}_x\text{FeO}_{3-\delta}$ for $x=0.1$ (a), 0.2 (c), 0.3 (e) and 0.4 (g). Occupation fraction with temperature for $\text{Ba}_{1-x}\text{La}_x\text{FeO}_{3-\delta}$ for $x=0.1$ (b), 0.2 (d), 0.3 (f) and 0.4 (h).

Generally, the occupation fraction increases with increasing La fraction. This is because the oxygen vacancy concentration reduces with more La, according to the charge balance. Due to the limited number of cages for certain cases, such as c_4 and c_5 in $x=0.1$, the data shows rather high oscillations, as shown in

Figure S1b. Typically, the occupation fraction of Ba-rich cages decreases with temperature, while it increases with temperature for La-rich cages.

The temperature effects on the oxygen jump between different cages.



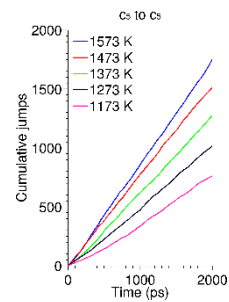


Figure S2. Temperature effects on the oxygen jump between different cages for $\text{Ba}_{0.5}\text{La}_{0.5}\text{FeO}_{3-\delta}$. Forward jump and back award jump are balanced. Therefore only one direction is shown.

Density functional theory calculations to determine the ground state of BaFeO₃ and La-doped BaFeO₃

Table S1. The relative energies (eV/f.u.) of ferromagnetic (FM), G-type antiferromagnetic (GAFM), A-type antiferromagnetic (AAFM) and C-type antiferromagnetic (CAFM) states, obtained by subtracting the energies of FM state. The ground state is marked in bold. The number in the parenthesis indicate the spin (μ_B). The lattice parameter of the cubic FM state is indicated in a (Å).

	FM	GAFM	AAFM	CAFM	a
BFO, 3.97 Å	0 (4.120)	0.273	0.082	0.153	3.97
BFO, relaxed	0 (4.156)	0.266	0.139	0.211	4.01
1/8 La BFO	0 (4.129)	0.220	0.076	0.128	3.99
1/4 La BFO	0(4.250)	0.191	0.066	0.106	3.98

O₂ binding energy correction

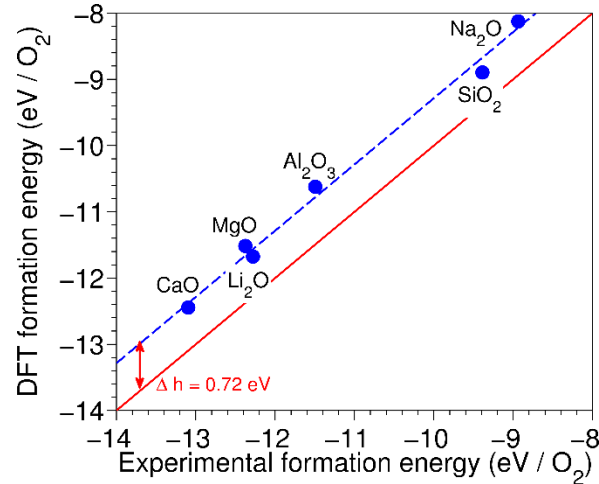


Figure S3. DFT-computed formation energy compared with experimental formation energy. An constant offset can be added to the DFT O₂ energy to correct this difference.¹

As shown in Figure S3, 0.72 eV is obtained to correct the DFT computed energy for O₂.

Cation configuration of BFO and La-substituted BFO

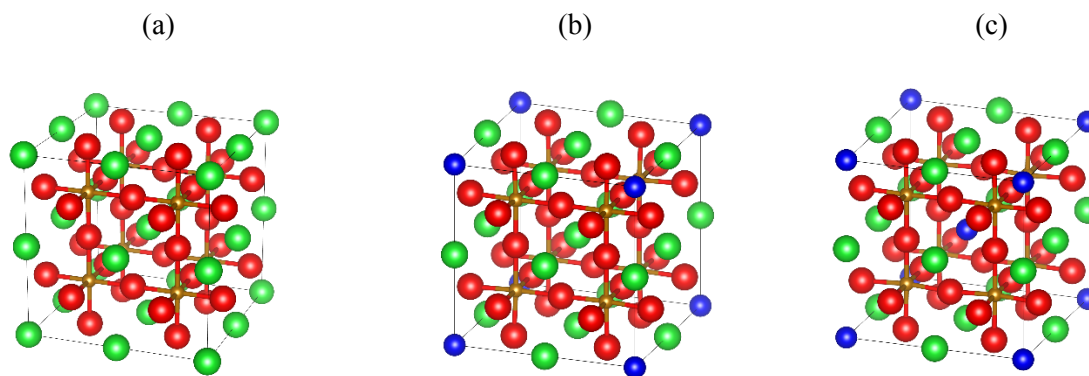


Figure S4. Cation configuration of BaFeO_3 (a), $\text{Ba}_{0.875}\text{La}_{0.125}\text{FeO}_3$ (b) and $\text{Ba}_{0.75}\text{La}_{0.25}\text{FeO}_3$ (c). Green, yellow, red and blue balls indicate Ba, Fe, O and La, respectively.

Vacancy formation energy and migration barrier

Table S2. Vacancy formation energies (eV) and migration barriers (eV) of BaFeO₃ and Ba_{0.875}La_{0.125}FeO₃.

	BaFeO ₃	Ba _{0.875} La _{0.125} FeO ₃
Vacancy formation energy with different A-site coordination	0.90 (BaBaBaBa)	1.36 (BaBaBaBa)
		1.14 (BaBaBaLa)
Oxygen migration barrier	0.69 (BaBaBaBa to BaBaBaBa)	0.87 (BaBaBaBa to BaBaBaBa)
		0.45 (BaBaBaLa to BaBaBaLa)
		0.97 (BaBaBaBa to BaBaBaLa)

References

1. Y.-L. Lee, J. Kleis, J. Rossmeisl and D. Morgan, *Physical Review B*, 2009, 80, 224101.