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# Supporting Information

## Harnessing Point-defect Induced Local Symmetry Breaking in the Tetragonal-$HfO_2$ System through Sterically Mismatched Ion Doping

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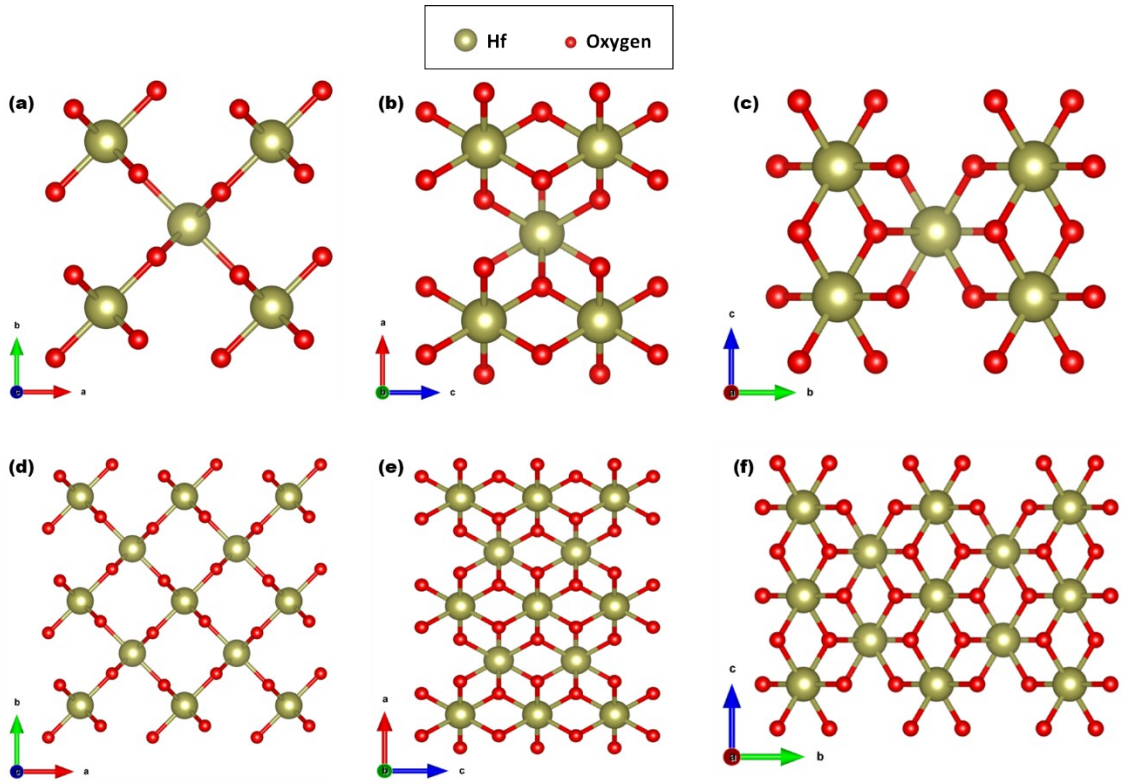


**Fig. S1** Figure presenting the (a-c) unit cell of the host material (tetragonal-HfO2, mp-776532), and the pristine 2x2x2 supercell structure. For clarification purposes, the Hf and the O-ions were indicated by golden and red, respectively.

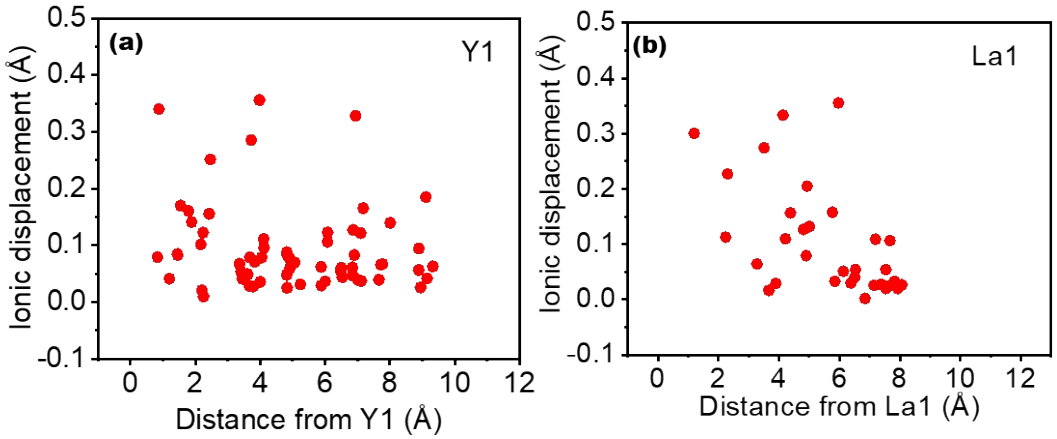


**Fig. S2** DFT-based first principal calculations of local defects structure in bulk with 2x2x2 supercell structure, where Y-ions and La-ions were doped as a defect. Ionic displacements relative to pure $HfO_2$ as a function of radial distance from the selected Y1-ion (a) and La1-ion (b) as a defect lies within ~11 Å from corresponding defects.

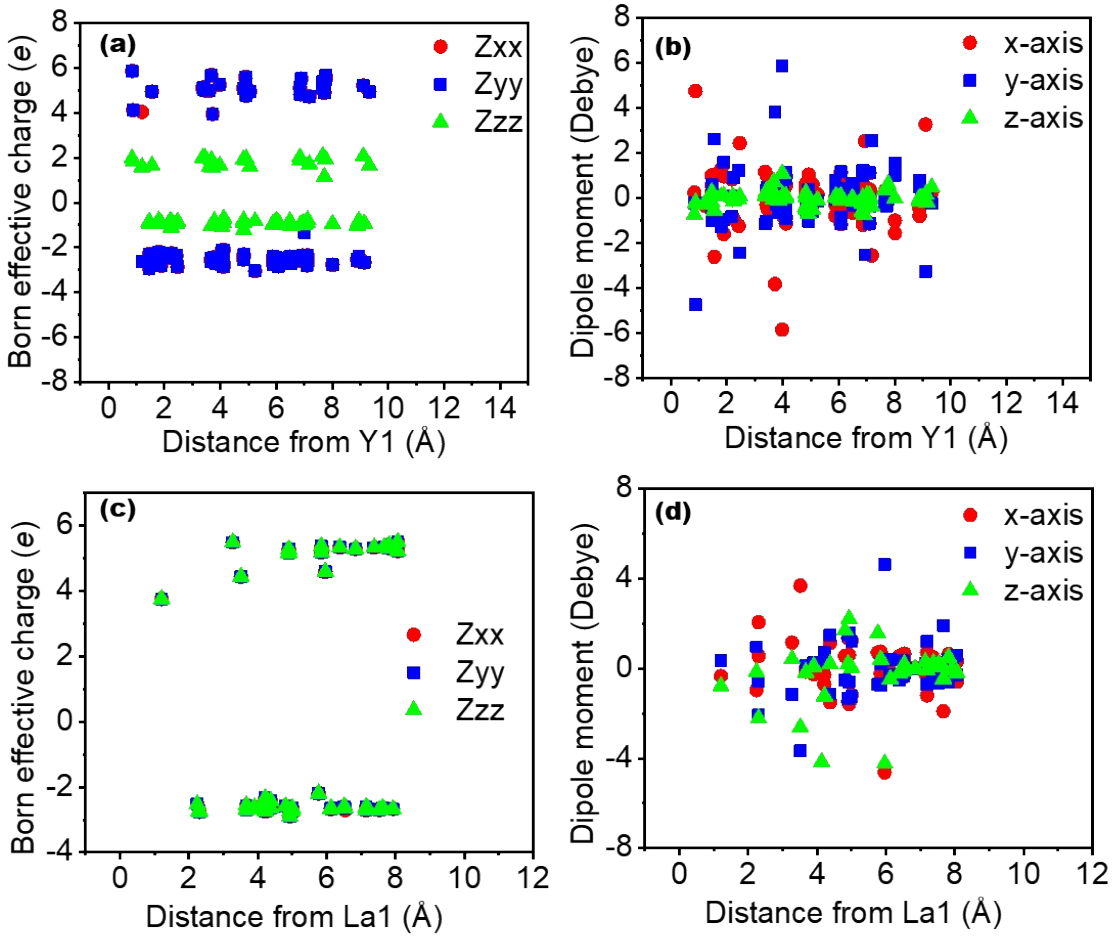


**Fig. S3** Born-effective charges (a and c) and Dipole moment (b and d) vs distance from defect (only Y1 and La1 was taken into consideration) were also calculated based on Density Functional Perturbation Theory (DFPT) calculations.

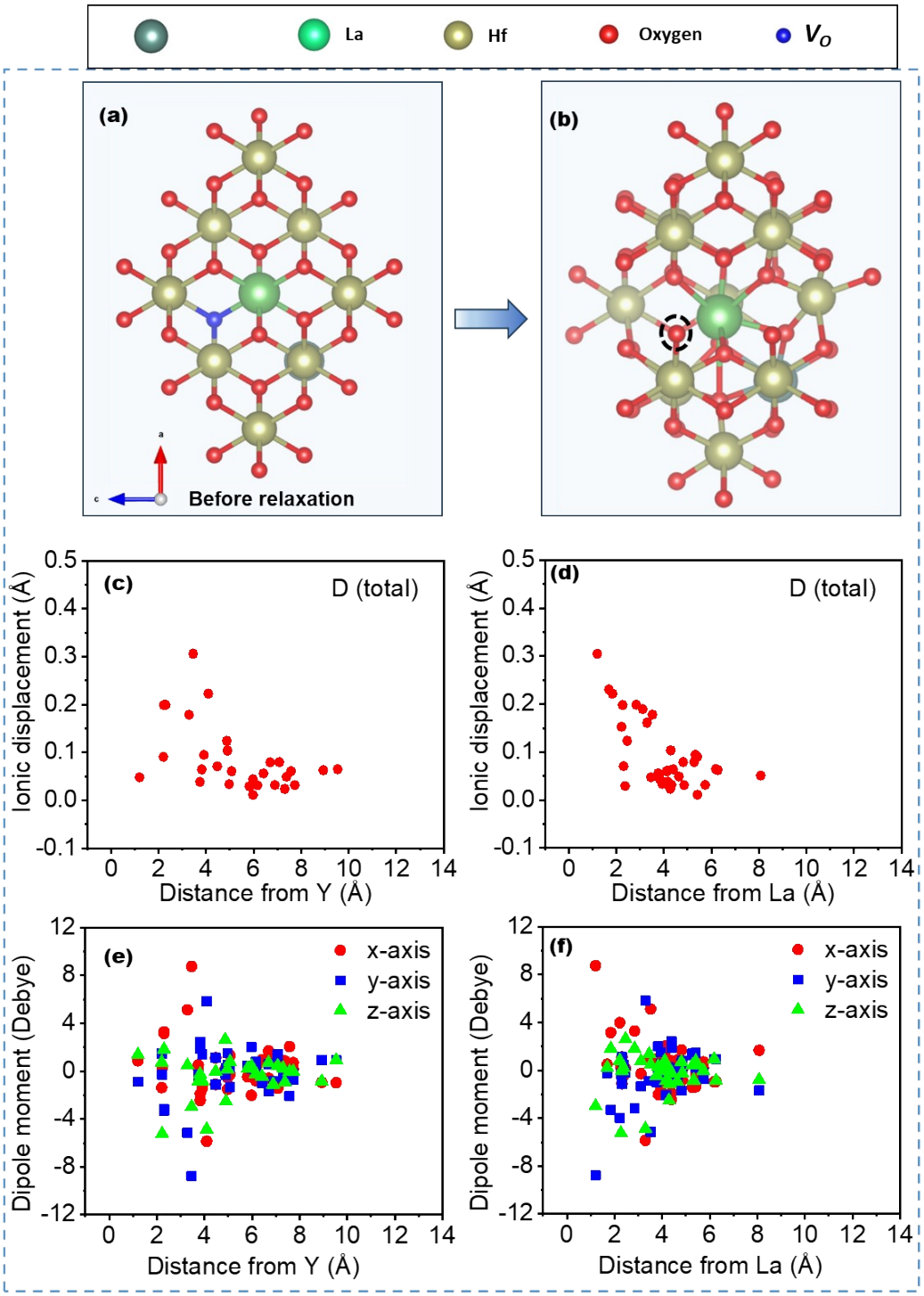


**Figure S4** DFT-based first principal calculations of local defects structure, where Y-ions and La-ions were co-doped as a defect in $HfO_2$, based on the defect structure presented in Figure 5c. (a) the structure before relaxation and the (b) the dopant-induced defect structures showing significant

ionic displacements were presented. Ionic displacement as a function of radial distance from the selected dopant (c) Y and (d) La as a defect lies within ~8 and 10 Å from corresponding defects, respectively. (where "D" represents total ionic displacement in all directions ($x$+$y$+$z$)). The calculated Dipole moment vs distance from defect (e) Y and (f) La were also presented.

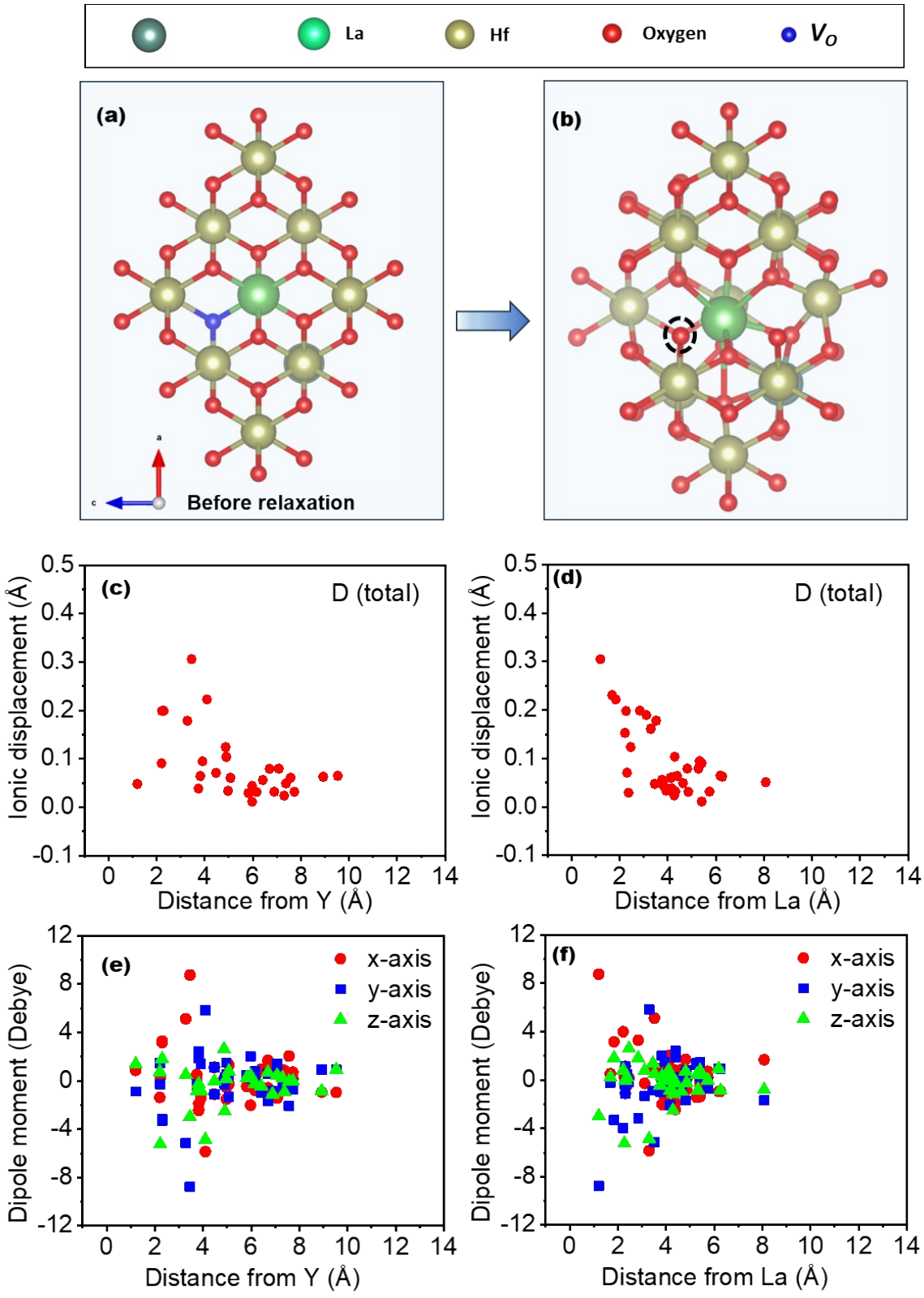
La
Hf
Oxygen
$V_O$
(a)
(b)
Before relaxation
(c)
D (total)
Ionic displacement (Å)
Distance from Y (Å)
(d)
D (total)
Ionic displacement (Å)
Distance from La (Å)
(e)
x-axis
y-axis
z-axis
Dipole moment (Debye)
Distance from Y (Å)
(f)
x-axis
y-axis
z-axis
Dipole moment (Debye)
Distance from La (Å)

**Figure S5** DFT-based first principal calculations of local defects structure, where Y-ions and La-ions were co-doped as a defect in $HfO_2$, based on the defect structure presented in Figure 5c. (a) the structure before relaxation and the (b) the dopant-induced defect structures showing significant ionic displacements were presented. Ionic displacement as a function of radial distance from the selected dopant (c) Y and (d) La as a defect lies within ~8 and 10 Å from corresponding defects, respectively (where "D" represents total ionic displacement in all directions ($x$+$y$+$z$)). The calculated Dipole moment vs distance from defect (e) Y and (f) La were also presented.