

## Supplementary Information for

# “Dopants Promoting Ferroelectricity in Hafnia: Insights From A Comprehensive Chemical Space Exploration”

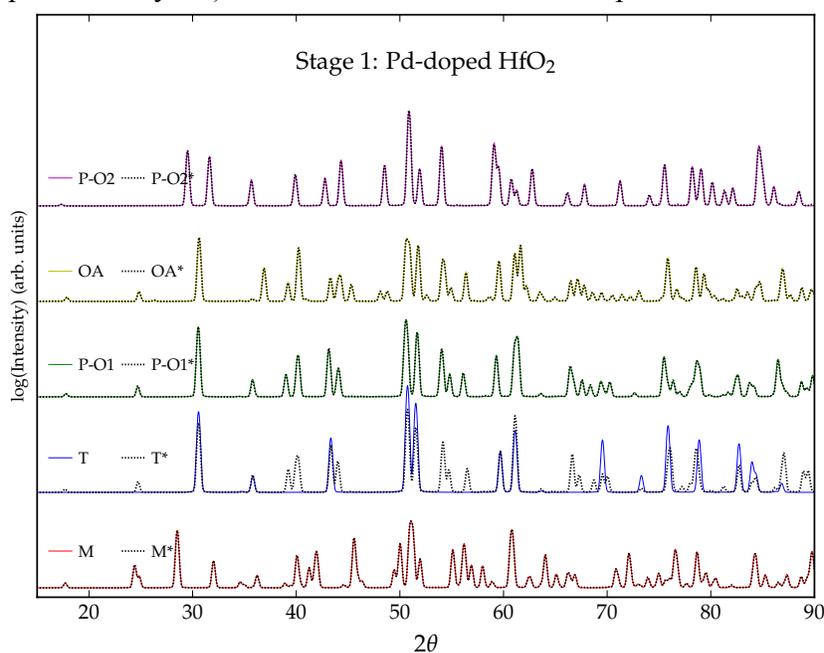
by

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### 1) Structural characterization

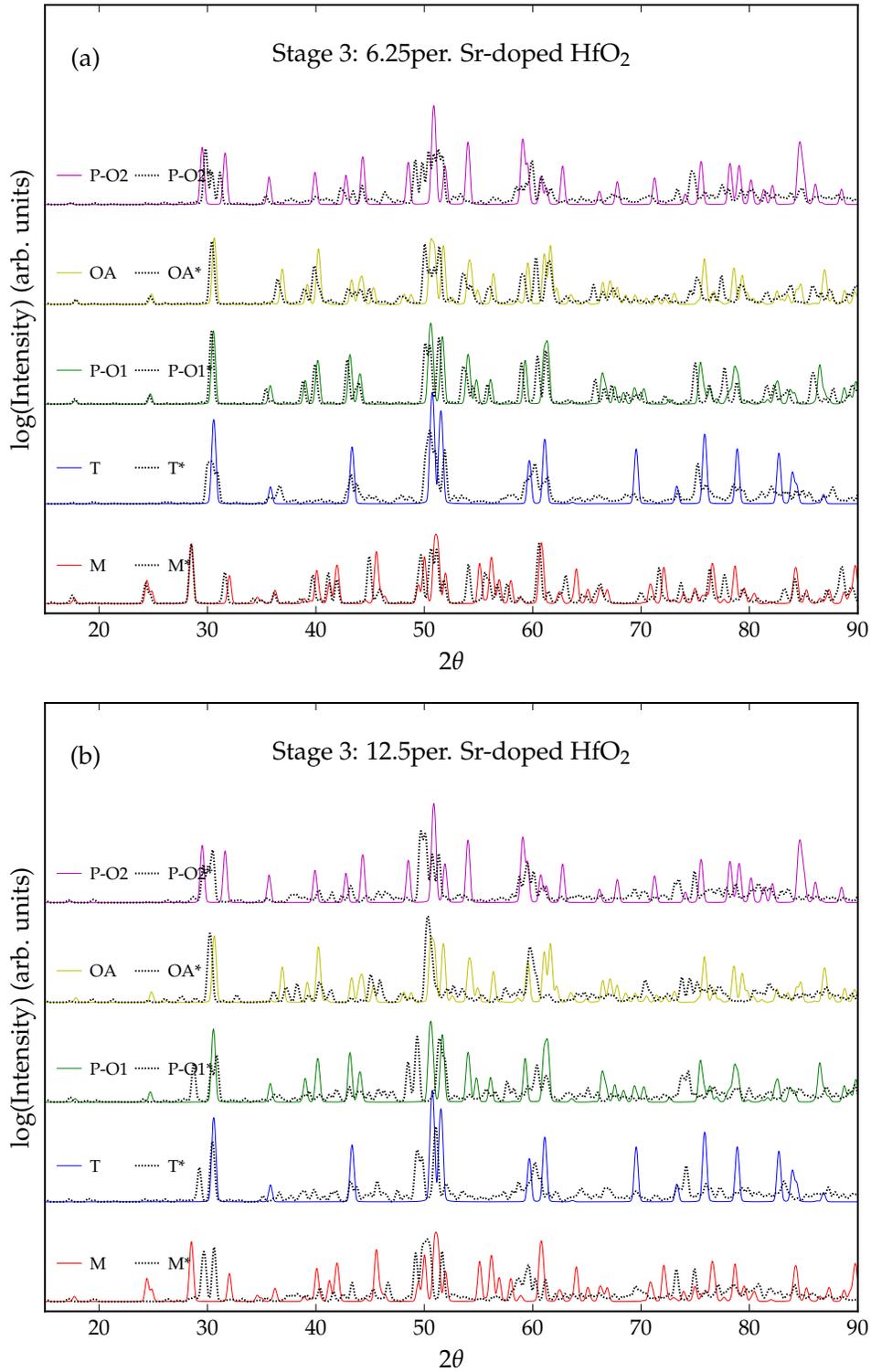
Simulated x-ray diffraction patterns were investigated to characterize different doped structures of hafnia obtained from our computations. In order to avoid discrepancies due to the identity of the dopant atom, in all the relaxed structures obtained from DFT calculations, the dopant atom(s) was/were replaced by Hf atom(s). Fullprof software<sup>1</sup> with default settings ( $\lambda=1.56 \text{ \AA}$ ) in the powder diffraction mode was used.

**A) Collapse of the T phase to the P-O1 phase:** Throughout this work several instances were noted when the T phase collapsed into the P-O1 phase upon dopant introduction. Figure S1 captures one of such examples for the case of Pd-doped hafnia in Stage 1 (see main article for details). Note that the peaks for the doped T phase (represented by T\*) best matches that of the P-O1 phase.



**Figure S1: Simulated x-ray diffraction patterns for different phases of pure and Pd-doped (marked with ‘\*’) hafnia under the conditions of Stage 1, as specified in the main article. While for the case of the M, P-O1, OA and P-O2 phases, the diffraction pattern corresponding to the doped state lie on top of that of the pure state, in the case of the T phase, the doped structure pattern matches best with that of the P-O1 phase instead of that of the pure T phase.**

**B) Loss of structural identity at higher doping concentrations:**



**Figure S2: Simulated x-ray diffraction patterns for different phases of pure and Sr-doped (with \*) hafnia at doping concentrations of (a) 6.25% and (b) 12.5% under the conditions of Stage 3, as specified in the main article. Except the case of 6.25% Sr-doped M, P-O1 and OA phases, the remaining doped structures are too different to be unambiguously characterized as any of the considered hafnia phase.**

In contrast to the previously discussed situations in which T phase upon doping relaxed into the P-O1 phase, we also encountered cases (see Fig. 4 of main article) when it was difficult to clearly characterize a doped hafnia phase after relaxation. Below we show examples of 6.25% and 12.5% Sr-doped hafnia in Figure S3. While at 6.25% doping concentration, the M, P-O1 and OA phases displayed their intensity peaks at positions of their corresponding pure phase, at higher doping concentration of 12.5%, none of the phases showed peaks at their respective pure phase positions, from which we conclude that these phases lose their structural identity at such doping concentrations. Also, the noticeable systematic shift in the peak positions of the doped M, P-O1 and OA phases, with respect to their corresponding pure phase positions, in Figure S2(a) is due to the volume expansion caused by the dopant.

## 2) Need for oxygen vacancy ( $O_{vac}$ )

In order to determine if  $O_{vac}$  need to be introduced to achieve charge neutrality in the case of dopants selected from Stage 1, we investigated the electronic structures of such systems obtained from calculations of Stage 1. For instance, in Figure S3, we plot the electronic energy diagram of the M phase of hafnia in pure bulk and doped state (corresponding to Stage 1 conditions). The presence of holes in the valence band in case of the various dopants, such as Ca, Sr, Y, etc., indicates the necessity to introduce  $O_{vac}$ , while the absence of a defect state in the case of Zr-doped system suggests that there is no requirement for  $O_{vac}$ . Similarly, the electronic structures of the M phase (see Figure S4) doped with 3.125% of divalent dopants and in presence of relevant charge neutralizing single  $O_{vac}$  (i.e., conditions of Stage 2) further establish this point.

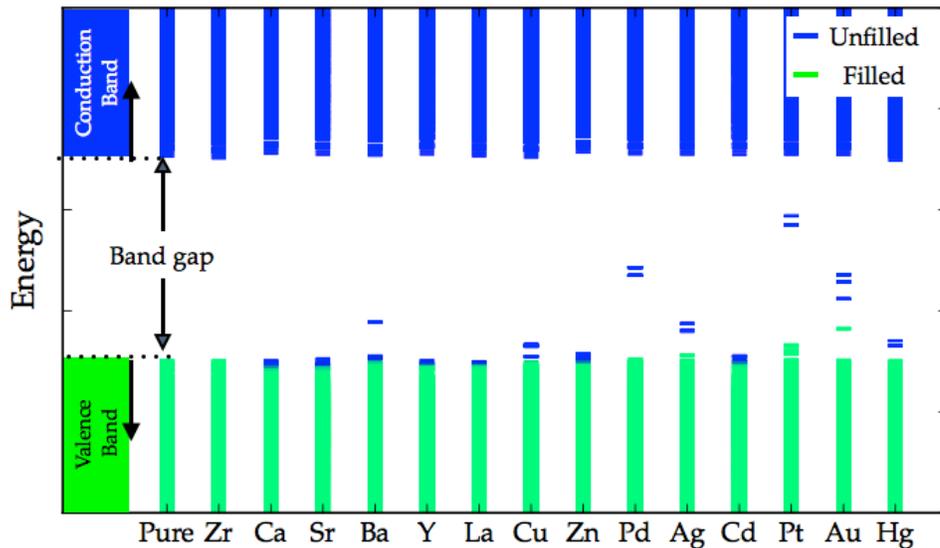


Figure S3: Electronic structure of the M phase of hafnia in pure bulk and doped state (with doping concentration of 3.125%). These results correspond to structures obtained under conditions imposed in Stage 1 (see main article for details). Green and blue symbols represent the filled and unfilled electronic states, respectively.

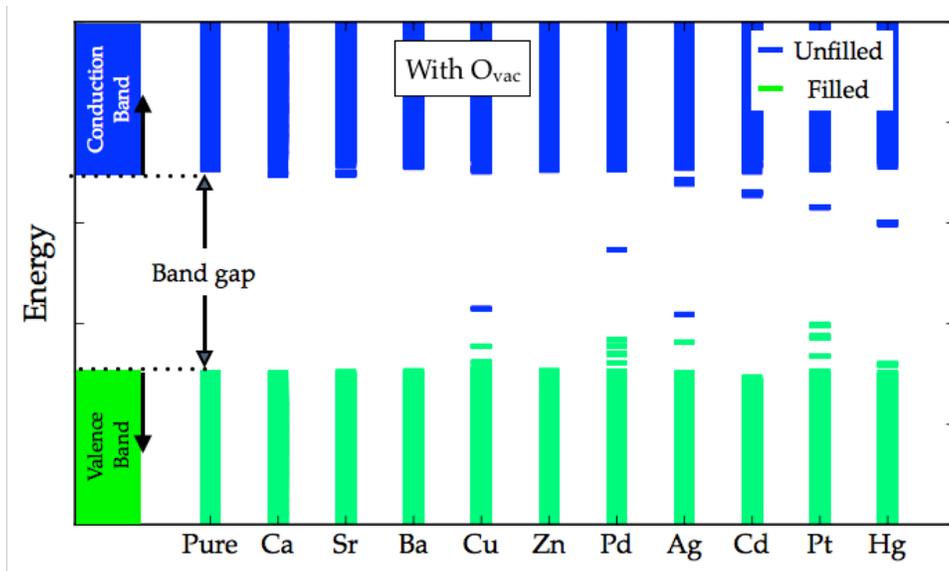


Figure S4: Electronic structure of the M phase of hafnia in pure bulk (without  $O_{vac}$ ) and doped state (with doping concentration of 3.125% and in presence of one  $O_{vac}$ ). These results correspond to structures obtained under conditions imposed in Stage 2 (see main article for details). Green and blue symbols represent the filled and unfilled electronic states, respectively.

#### References:

[1] Rodriguez-Carvajal J., Physica B, 192, 55(1993). The complete program and documentation can be obtained at <http://www.ill.eu/sites/fullprof/>