

Supplementary Information for “Computational study of hydrogen doping induced metal-to-insulator transition in CaFeO_3 , SrFeO_3 , BaFeO_3 and SmMnO_3 ”

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1. H sites searching

As the previous work for SmNiO_3 has shown¹, the stable H sites searching started with the single stable hydrogen atom site. There were two Ni-O layers in the unit cell, with two Ni atoms in each Ni-O layer. The goal is to find four most stable sites in the Ni-O (001) plane. Thus, the test of stable four H sites configuration was achieved by placing two hydrogen atoms at each Ni-O layer. This leads to a combination of $C_4^2 \times C_4^2 = 36$ configurations in the unit cell. After the geometry optimization, the most stable site was selected. Since the atomic sizes and lattice structures of the perovskites in this study are different from SmNiO_3 , the ground state H sites configurations could be different.

CaFeO_3 and SmMnO_3 have the same space group ($Pbnm$) as SmNiO_3 does. Thus, the fractional coordinates of hydrogen atoms of 36 configurations from SmNiO_3 were taken to further optimize at the level of PBEsol+4 to search for the most stable configurations for CaFeO_3 and SmMnO_3 . It turned out that configurations #3 and #34 have the lowest energy for H: SmMnO_3 , and these two configurations are the second and third most stable configurations for H: SmNiO_3 .¹ The #34, 0.0009 eV lower in energy than #3, is chosen for the electronic structure calculations. The relative energy referenced to the #34 is plotted in the Fig. S1.

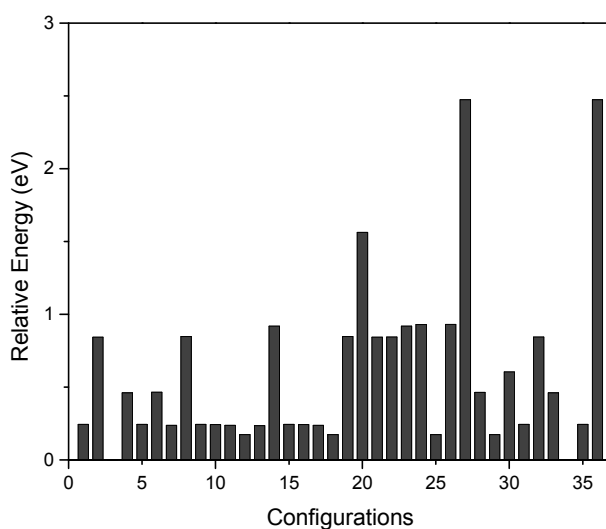


Figure S1. Relative energy of 36 configurations of H sites for H: SmMnO_3 . The energy values are referenced to #34.

The structures of configurations #3 and #34 were checked since their energy difference is so small. The side view of #3 and #34 are shown in the Fig. S2. H atoms are bonded to oxygen atoms within the Mn-O layer, and head vertically toward the interstitial sites around Sm-O layers. These two configurations are actually equivalent with different orientations of the unit cell vectors.

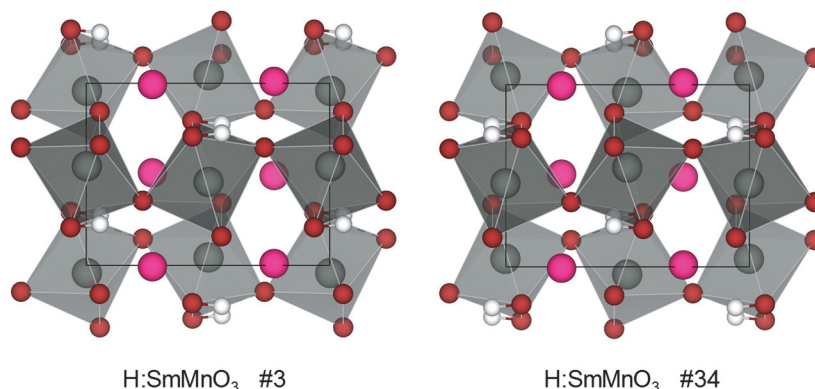


Figure S2. Structures of configurations #3 and #34 for H:SmMnO₃. Color code: Sm - pink, Mn - gray, O - red, H - white.

For CaFeO₃, the same method was applied and the relative energy difference is shown in the Fig. S3. Similar to SmMnO₃, the #3 and #34 have the lowest energy. The energy of #34 is only 0.0003 eV higher than #3. The configuration #3 was chosen for further calculations of electronic structures.

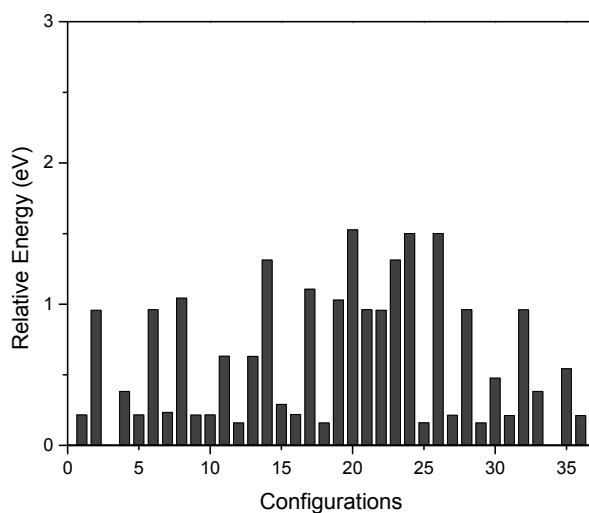


Figure S3. Relative energy of 36 configurations of H sites for H:CaFeO₃. The energy values are referenced to #3.

For SrFeO₃ and BaFeO₃, the 36 configurations are not proper for describing the potential stable H sites, because both perovskites have a cubic structure with the symmetry group $Pm\bar{3}m$, which is different from $Pbnm$ SmNiO₃. The 36 configurations used above would introduce

unreasonable initial H sites. Hence, the stable sites for single H atom were tested and they are shown in the Fig. S4a. The hydrogen atoms are located at the Fe-O layer bonded to O atoms. Putting two H in the first layer, as shown in Fig. S4b, breaks the cubic symmetry of the perovskite. The remaining two H can be located at any two of the eight possible sites shown in Fig. S4a. Thus, there are $C_8^2 = 28$ different configurations for the second layer, which means that there are $4 \times 28 = 112$ possible configurations in the SrFeO_3 unit cell. After applying geometry optimization of the 112 cases, the relative energy can be plotted and shown in Fig. S5. Configuration #14 is the most stable one and applied for further calculations with H:SrFeO_3 . For the BaFeO_3 , the initial H sites were taken from the optimized 112 configurations for H:SrFeO_3 and then further optimized. The results show that configuration #61 is with the lowest energy for H:BaFeO_3 , which is also one of the low energy configurations for H:SrFeO_3 . The relative energy for H:BaFeO_3 are shown in Fig. S6.

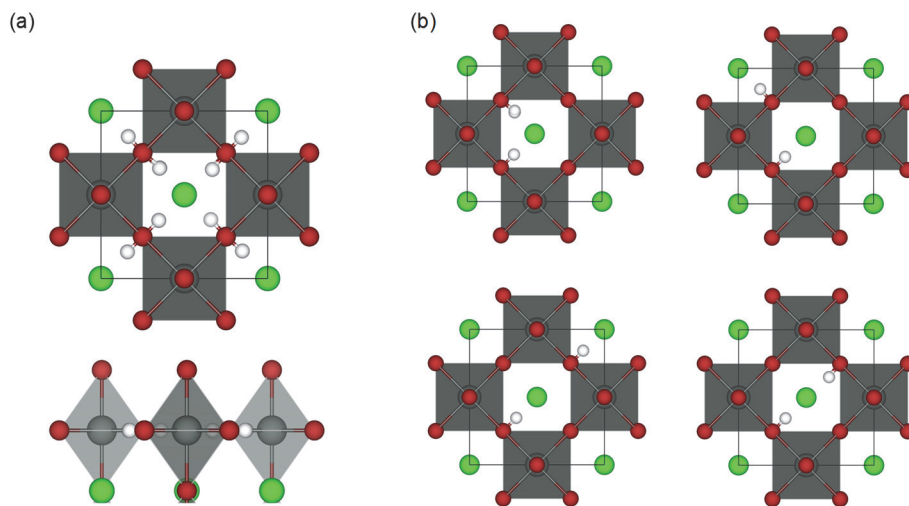


Figure S4. (a) Stable H sites for single hydrogen in SrFeO_3 . (b) Possible combinations for two H sites in one Fe-O layer in SrFeO_3 . Color code: Sr - green, Fe - gray, O - red, H - white.

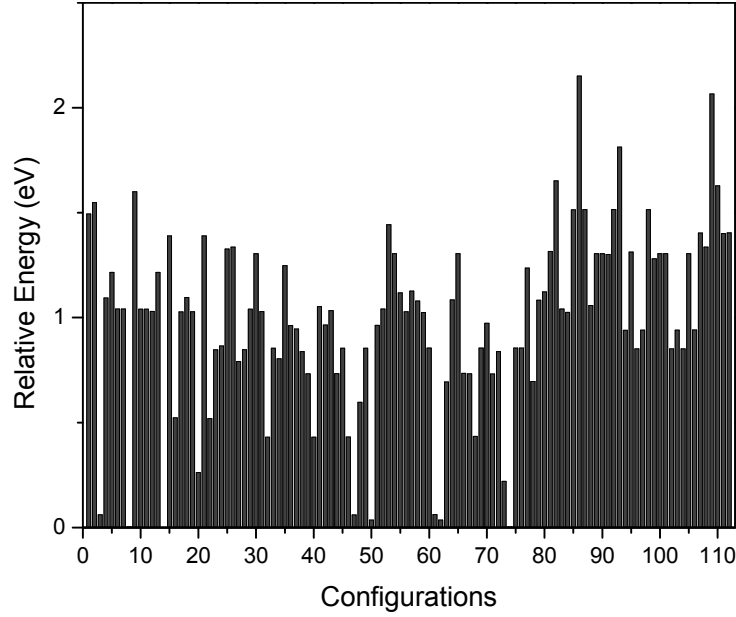


Figure S5. Relative energy of 112 configurations of H sites for H:SrFeO₃. The energy values are referenced to #14.

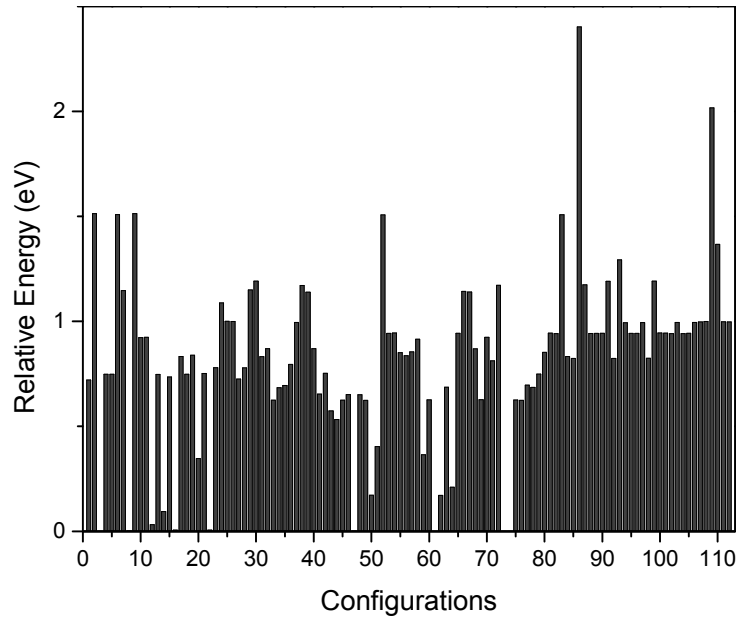


Figure S6. Relative energy of 112 configurations of H sites for H:BaFeO₃. The energy values are referenced to #61.

2. Valance band maximum (VBM) and conduction band minimum (CBM) for CaFeO₃

In the proposed MIT mechanism, the hydrogen atoms will provide electron to the Fe empty e_g orbital, so that all of the t_{2g} and e_g orbitals are singly occupied. The strong Coulomb repulsion from $3d$ electrons on those singly occupied orbitals will prevent the electron from moving freely. To verify if the Fe e_g orbital truly accept the electron after doping, we plot the density of electrons

within 100 meV below VBM and 100 meV above CBM in Figure S7. In pure CaFeO₃, the VBM electron density on Fe is of hybridized 3d states, with features of a $d_{x^2-y^2}$ (lobes along Fe-O bonds in the top view), while the CBM electron density of Fe has d_{z^2} character, with an elongated octahedron along the *c* direction. This is in agreement with one of the e_g orbital occupied and the other unoccupied. After the H doping, the VBM electron density on Fe is very similar to the CBM of pure CaFeO₃, while the CBM electron density on Fe looks like a $t_{2g} d_{xy}$ orbital (lobes along the empty space between Fe-O bonds in the top view). This indicates that the additional electrons fill the previously empty e_g orbitals and the next available states on Fe are now the t_{2g} state.

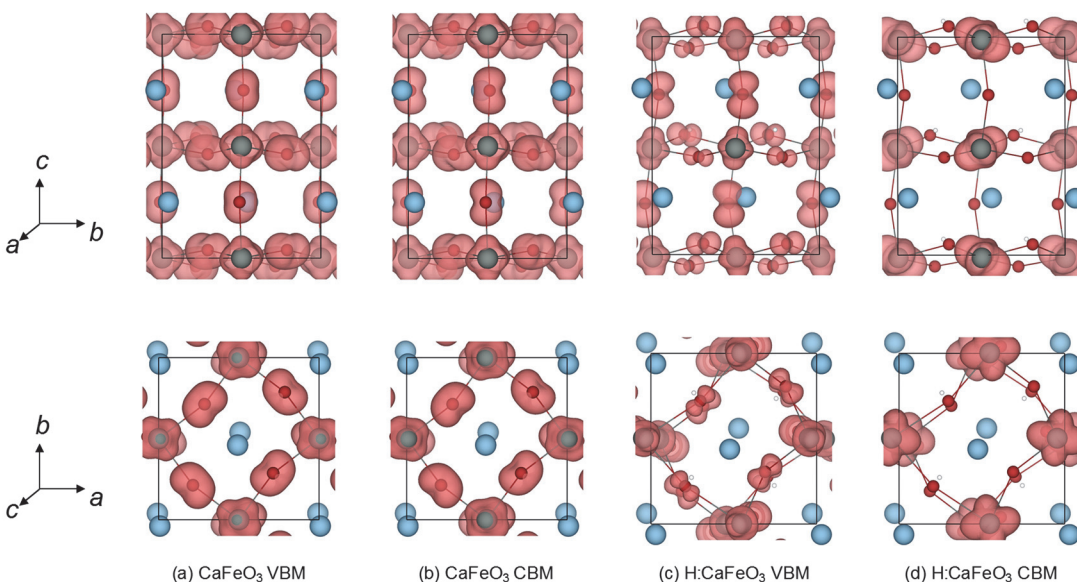


Figure S7. Side views (first row) and top views (second row) of (a) VBM and (b) CBM of pure CaFeO₃ and (c) VBM and (d) CBM of H:CaFeO₃. The isosurface value is 0.0004 e/Bohr³. Color code: Ca - blue, Fe - grey, O - red, H - white.

Reference

- 1 P. Yoo and P. Liao, *Mol. Syst. Des. Eng.*, 2018, **3**, 264–274.