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


**Supporting Information for**

# A Combined Computational and Experimental Investigation of Mg Doped α-$Fe_2O_3$

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Details of the pseudopotentials, provided with the VASP package, used in this study:

**Fe atom**

TITEL = PAW_PBE Fe_pv 06Sep2000
ENMAX = 293.238; ENMIN = 219.929 eV
ZVAL = 14.000

**O atom**

TITEL = PAW_PBE O 08Apr2002
ENMAX = 400.000; ENMIN = 300.000 eV
ZVAL = 6.000

**Mg atom**

TITEL = PAW_PBE Mg_pv 06Sep2000
ENMAX = 265.574; ENMIN = 199.180 eV
ZVAL = 8.000

**Ba atom**

TITEL = PAW_PBE Ba_sv 06Sep2000
ENMAX = 187.181; ENMIN = 140.386 eV
ZVAL = 10.000

Table S1a. Comparison of geometrical parameters (Å, $Å^3$) and total energies (eV) using 500eV and 700 eV cutoffs, hexagonal cells of pure $Fe_2O_3$.

| | | E | V | a | b | c |
|---|---|---|---|---|---|---|
| 30 atoms | 500 | -206.526 | 313.560 | 5.097 | 5.097 | 13.937 |
| | 700 | -206.772 | 312.910 | 5.092 | 5.092 | 13.933 |
| 60 atoms | 500 | -413.055 | 627.120 | 5.097 | 10.193 | 13.938 |
| | 700 | -413.551 | 625.600 | 5.092 | 10.184 | 13.929 |
| 120 atoms | 500 | -826.119 | 1254.180 | 10.193 | 10.193 | 13.939 |
| | 700 | -827.114 | 1251.200 | 10.184 | 10.184 | 13.929 |

Table S1b. Comparison of average Fe and O Bader charges using 500eV and 700 eV cutoffs. Both cell parameters optimization and density calculations of hexagonal cells of pure $Fe_2O_3$ were performed with the 500eV and 700 eV cutoffs.

| | | Fe charge | O charge |
|---|---|---|---|
| 30 atoms | 500 | 1.780 | -1.186 |
| | 700 | 1.782 | -1.188 |

Table S2. Computed 60 atoms simulation cell of $\alpha$-$Fe_2O_3$ with 2 Mg atoms substituting 2 Fe atoms.

| 60 atoms | 2 Mg, 23Fe, 36O | E | V | a | b | c | Total magnetic moment of the simulation cell |
|---|---|---|---|---|---|---|---|
| | conf. a | -406.206 | 627.48 | 5.097 | 10.193 | 13.948 | 7.91 |
| | conf. b | -405.004 | 622.89 | 5.081 | 10.193 | 13.887 | 4.00 |
| | conf. c | -406.127 | 627.62 | 5.099 | 10.196 | 13.947 | 7.91 |
| | conf. d | -406.149 | 626.96 | 5.085 | 10.212 | 13.931 | 0.24 |
| | conf. e | -406.089 | 626.97 | 5.103 | 10.193 | 13.937 | 0.74 |
| | conf. f | -404.915 | 623.51 | 5.084 | 10.191 | 13.888 | 0.00 |
| | conf. g | -405.016 | 623.2 | 5.083 | 10.191 | 13.883 | 0.00 |

Table S3. Cell parameters and total energies of $Mg_xFe_{2-x}O_3$, x=0.17 (30 atoms simulation cell), x=0.08 (60 atoms simulation cell), x=0.04 (120 atoms simulation cell).

| | | E | V | a | b | c |
|---|---|---|---|---|---|---|
| 30 atoms | 1 Mg, 11Fe, 18O | -203.102 | 313.75 | 5.096 | 5.096 | 13.949 |
| 60 atoms | 1 Mg, 23Fe, 36O | -409.608 | 627.15 | 5.094 | 10.191 | 13.938 |
| 120 atoms | 1 Mg, 47Fe, 72O | -822.653 | 1254.20 | 10.194 | 10.194 | 13.937 |

Table S4. Bader partial charges for $M_{0.17}Fe_{1.83}O_3$, M=Fe, Mg, Ba.

| | **M=Fe** | **M=Mg** | **M=Ba** |
|---|---|---|---|
| Fe | 1.780 | 1.797 | 1.733 |
| **M** | **1.780** | **1.719** | **1.552** |
| Fe | 1.780 | 1.784 | 1.695 |
| Fe | 1.780 | 1.791 | 1.786 |
| Fe | 1.780 | 1.780 | 1.808 |
| Fe | 1.780 | 1.784 | 1.795 |
| Fe | 1.780 | 1.790 | 1.790 |
| Fe | 1.780 | 1.785 | 1.776 |
| Fe | 1.780 | 1.789 | 1.810 |
| Fe | 1.780 | 1.789 | 1.778 |
| Fe | 1.780 | 1.783 | 1.776 |
| Fe | 1.780 | 1.809 | 1.788 |
| O | -1.186 | -1.196 | -1.076 |
| O | -1.186 | -1.190 | -1.075 |
| O | -1.187 | -1.199 | -1.075 |
| O | -1.186 | -1.218 | -1.176 |
| O | -1.187 | -1.215 | -1.174 |
| O | -1.186 | -1.209 | -1.175 |
| O | -1.186 | -1.186 | -1.194 |
| O | -1.187 | -1.175 | -1.197 |
| O | -1.186 | -1.180 | -1.194 |
| O | -1.187 | -1.186 | -1.191 |
| O | -1.186 | -1.194 | -1.190 |
| O | -1.186 | -1.185 | -1.189 |
| O | -1.187 | -1.187 | -1.190 |
| O | -1.186 | -1.188 | -1.191 |
| O | -1.186 | -1.186 | -1.192 |
| O | -1.186 | -1.171 | -1.202 |
| O | -1.187 | -1.167 | -1.204 |
| O | -1.186 | -1.168 | -1.201 |

**Figure S1. Electronic Density of states of pure α-$Fe_2O_3$, using 700 eV cutoffs. Black – total DOS; Blue – Fe *d* states; Red – O *p* states. The Fermi energy is set to zero.**

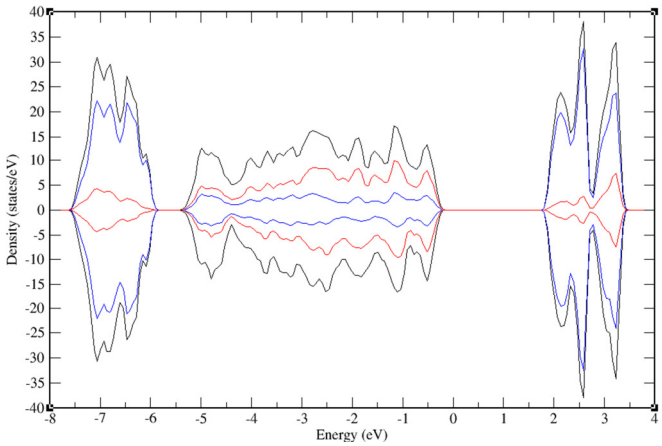
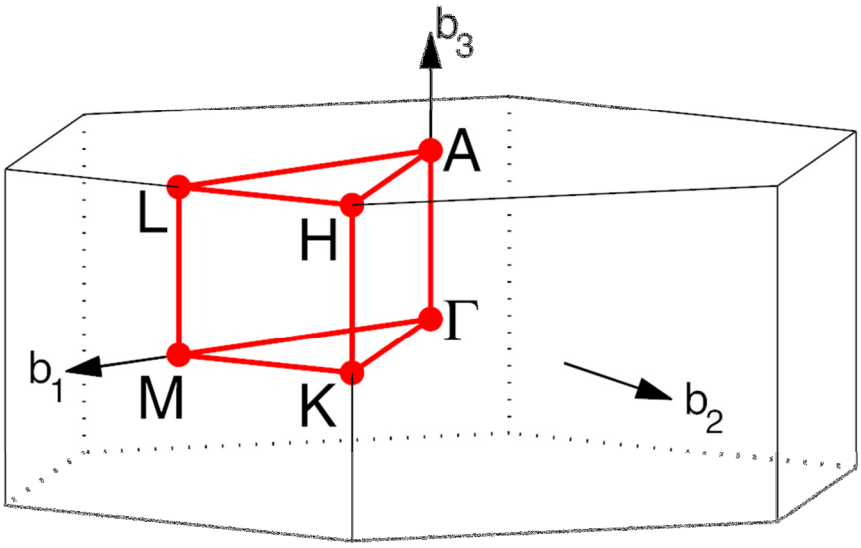



**Figure S2. The reciprocal lattice image and k-point path was generated with the ACONVASP facility, http://materials.duke.edu/awrapper.html.**




HEX path: Γ-M-K-Γ-A-L-H-A|L-M|K-H

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

**Figure S3. XRD of a point from the α-$Fe_2O_3$ library, showing the pure hematite phase.**

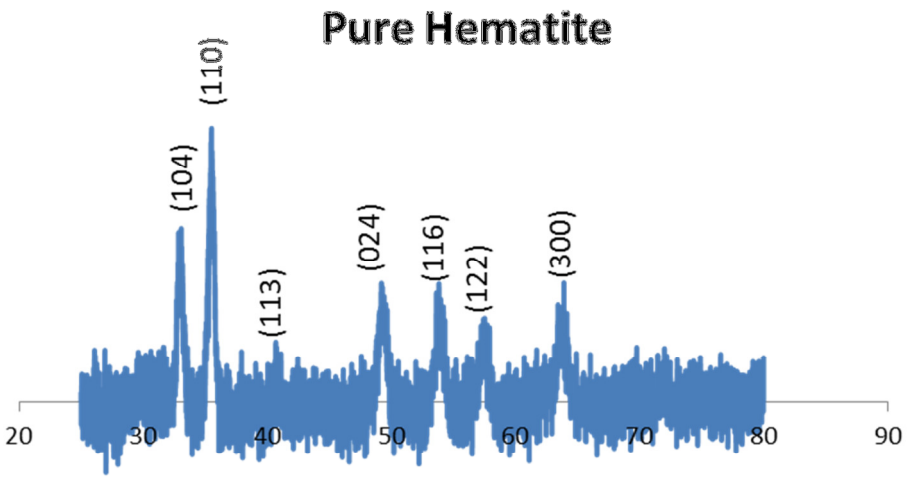



**Figure S4. Full bandgap maps of the a) pure hematite library, and b) $Fe_2O_3$-MgO library. The maps are set to the same scale bar, and indicate the bandgap reduction for the $Fe_2O_3$-MgO library.**

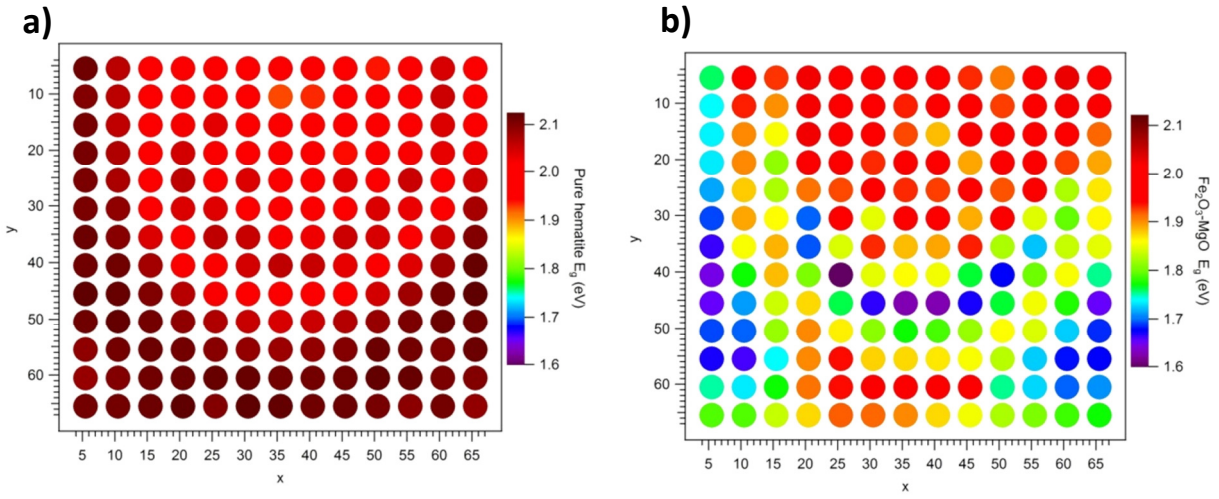


**Figure S5. a) Tauc plots for calculating the bandgap of hematite and of the Mg-$Fe_2O_3$ phases. b) Bandgap vs. Mg/Fe atomic ratio, showing a no change in the bandgap up to a ratio of Mg/Fe=0.2. For higher Mg/Fe ratios a reduction in the bandgap appears, arising from the newly formed phases.**

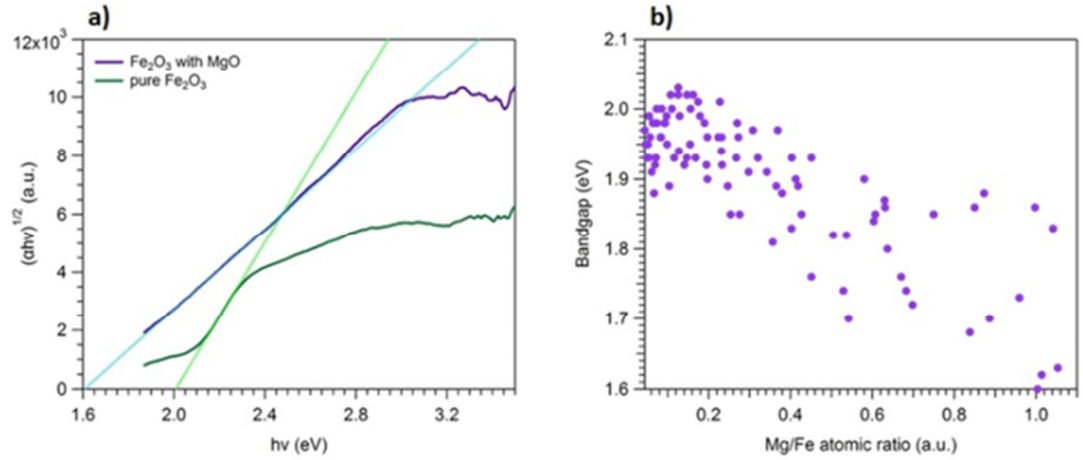



**Figure S6. Detailed electronic DOS of pure α-$Fe_2O_3$. Black – total DOS; Blue – Fe *d* states; Red – O *p* states. The Fermi energy is set to zero.**

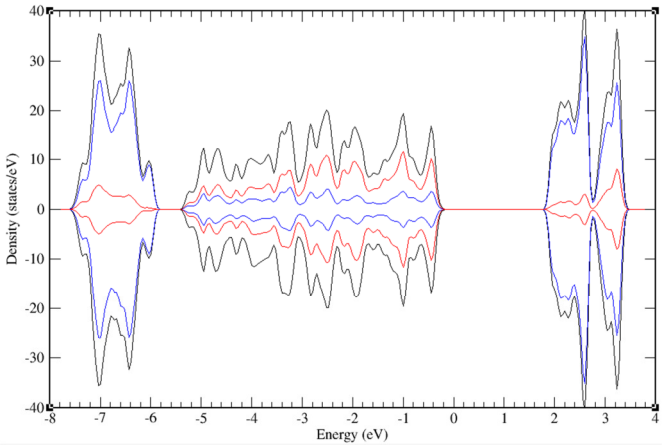


**Figure S7. Detailed electronic DOS of α-$Mg_{0.17}Fe_{1.83}O_3$. Black – total DOS; Blue – Fe, *d* states; Red – O, *p* states; Green – Mg, all states. The Fermi energy is set to zero.**

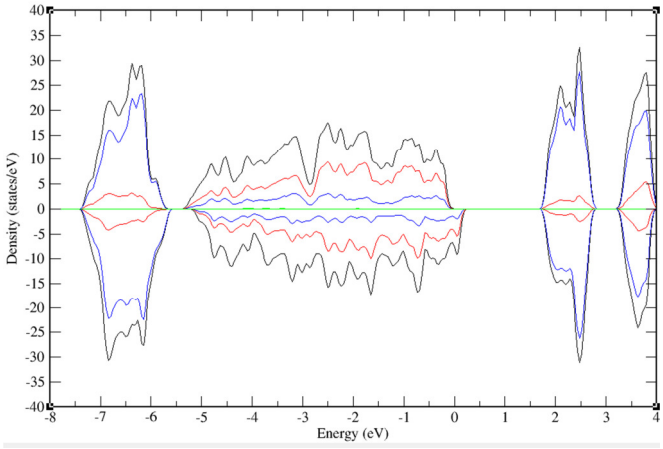



**Figure S8. Detailed electronic DOS of a hypothetical α-$Ba_{0.17}Fe_{1.83}O_3$. Black – total DOS; Blue – Fe, *d* states; Red – O, *p* states; Green – Ba, all states. The Fermi energy is set to zero.**

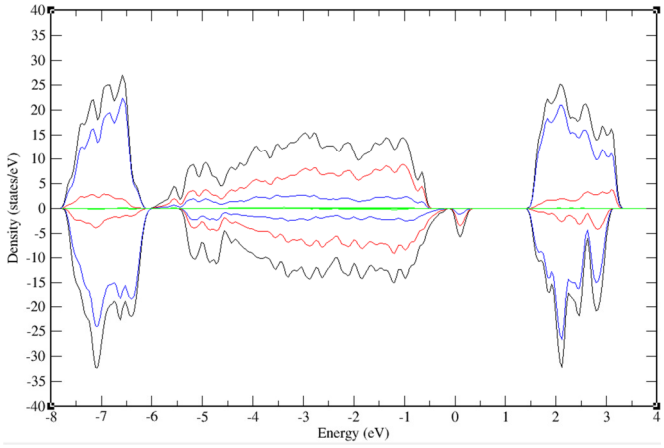


**Figure S9. A comparison of experimentally measured absorption coefficient and our calculated imaginary part of the macroscopic dielectric constant for $\alpha$-$Fe_2O_3$ (black) and $Mg_{0.17}Fe_{1.83}O_3$ (red).**