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

Electronic Supplementary Information

Regulation of Saturation Magnetization of Magnetite by Doping with Group III Elements

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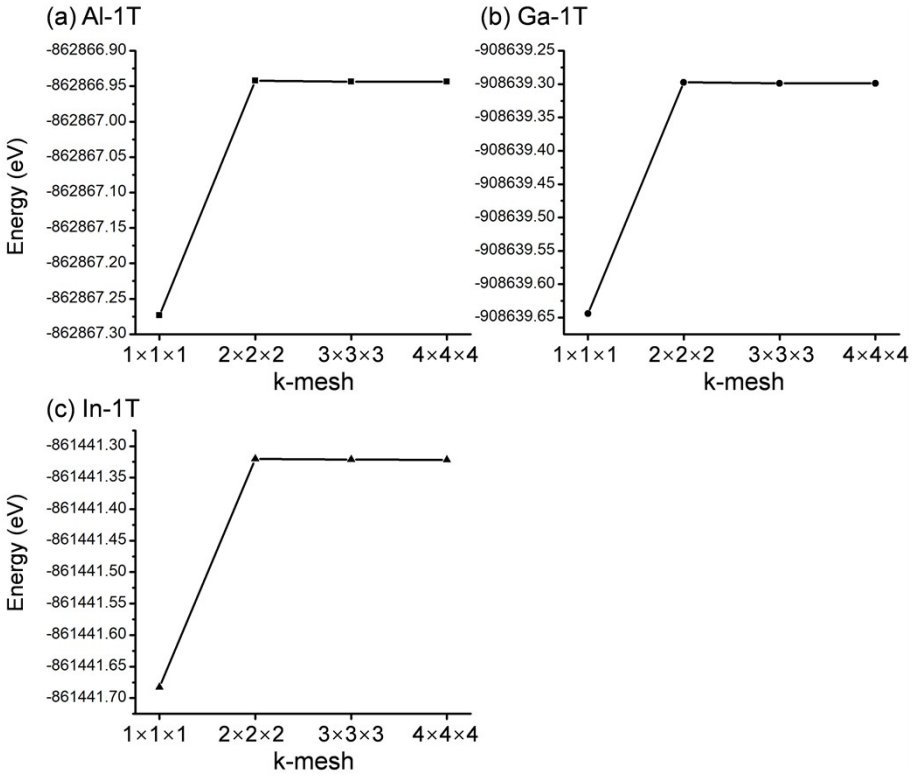

Figure S1. The total energy as a function of k-mesh sampling for doped Fe_3O_4: (a) one Al atom replacing one tetrahedral Fe atom; (b) one Ga atom replacing one tetrahedral Fe atom; (c) one In atom replacing one tetrahedral Fe atom. The results show that 3 × 3 × 3 k-mesh sampling is enough for convergence.

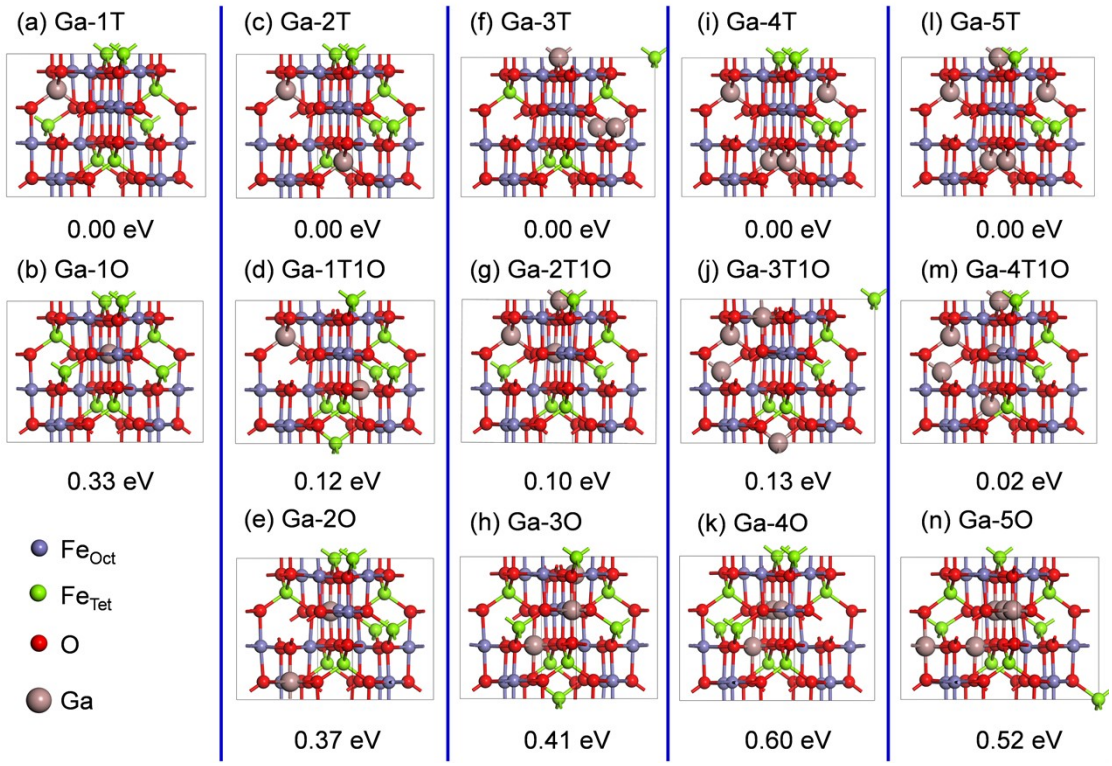

Figure S2. Optimized structures of Fe_3O_4 doped with different number of Ga atoms (from one to five). For each column, the number of doped Ga atoms is the same. At each doping concentration, the relative energy with respect to the case that all Ga atoms replace tetrahedral Fe atoms is listed below each structure. The label Ga-mTnO (m and n are integers) means that m Ga atoms replace Fe_{Tet} and n Al atoms replace Fe_{Oct}.

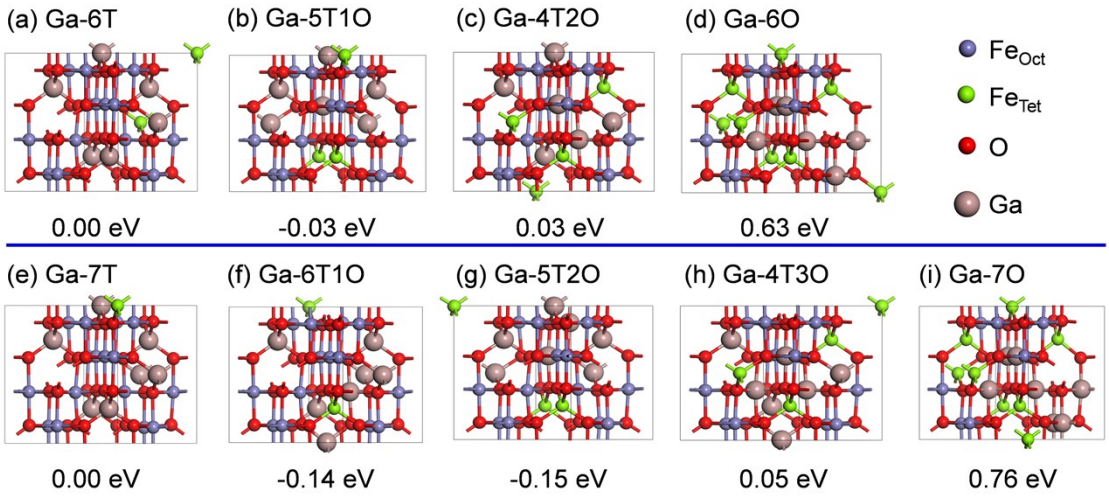

Figure S3. Optimized structures of Fe_3O_4 doped with different number of Ga atoms (from six to seven). For each column, the number of doped Ga atoms is the same. At each doping concentration, the relative energy with respect to the case that all Ga atoms replace tetrahedral Fe atoms is listed below each structure. The label Ga-mTnO (m and n are integers) means that m Ga atoms replace Fe_{Tet} and n Al atoms replace Fe_{Oct}.

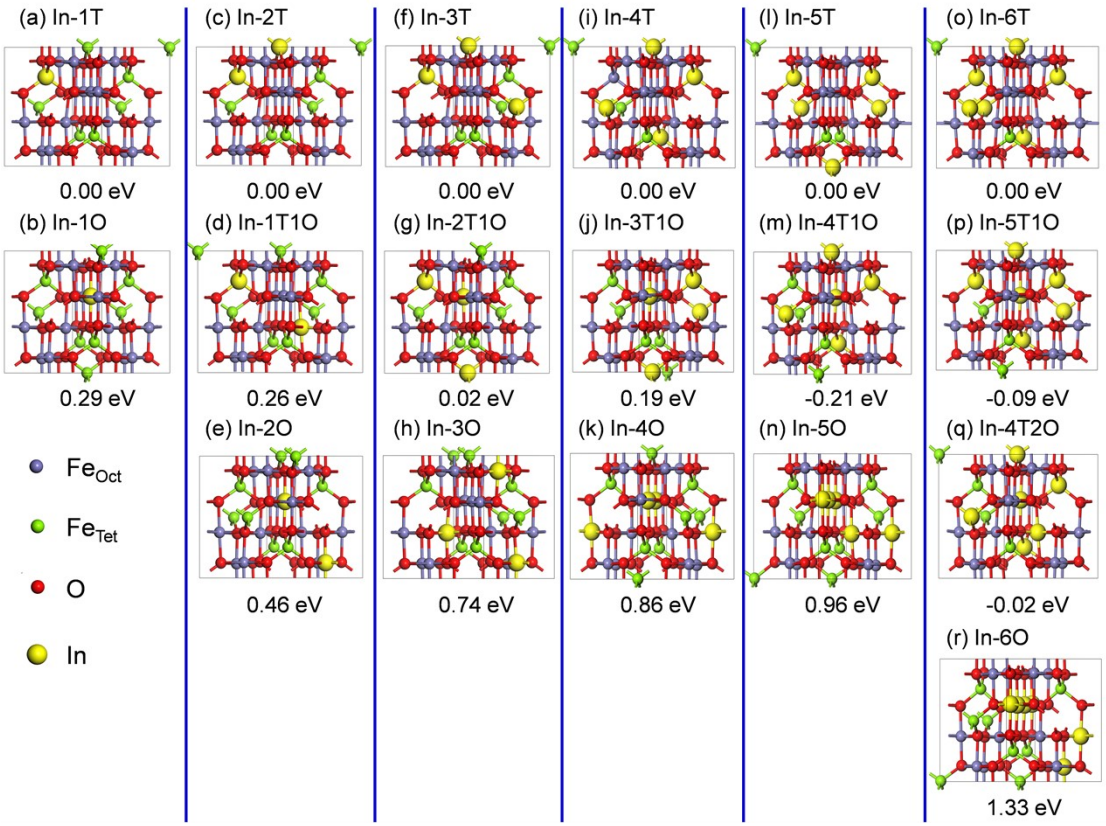

Figure S4. Optimized structures of Fe_3O_4 doped with different number of In atoms (from one to six). For each column, the number of doped In atoms is the same. At each doping concentration, the relative energy with respect to the case that all In atoms replace tetrahedral Fe atoms is listed below each structure. The label In-mTnO (m and n are integers) means that m In atoms replace Fe_{Tet} and n In atoms replace Fe_{Oct}.

For each configuration shown in Figure 2, S2, S3 and S4, several different structures were considered and the structure with the lowest energy was shown. For one dopant per cell, only one possible configuration for substituting Fe_{Tet} or Fe_{Oct}. For two dopants per cell, two configurations are considered for X-2T, X-1T1O and X-2O (X = Al, Ga, In), respectively. One case is that the two dopants are as close to each other and the other case is that the two dopants are far away from each other. For three and more dopants per cell, it is difficult to exhaust all configurations. Therefore, at least three configurations were chosen randomly. The energy difference ranges from a few meV to several tens of meV. In this case, we cannot guarantee the report configuration is the lowest energy configuration. However, the trend that at low concentration Al, Ga or In prefers tetrahedral sites and after a critical concentration, subsequent dopants prefer

octahedral sites should be correct (shown in Figure 3a, 5a and 5c).

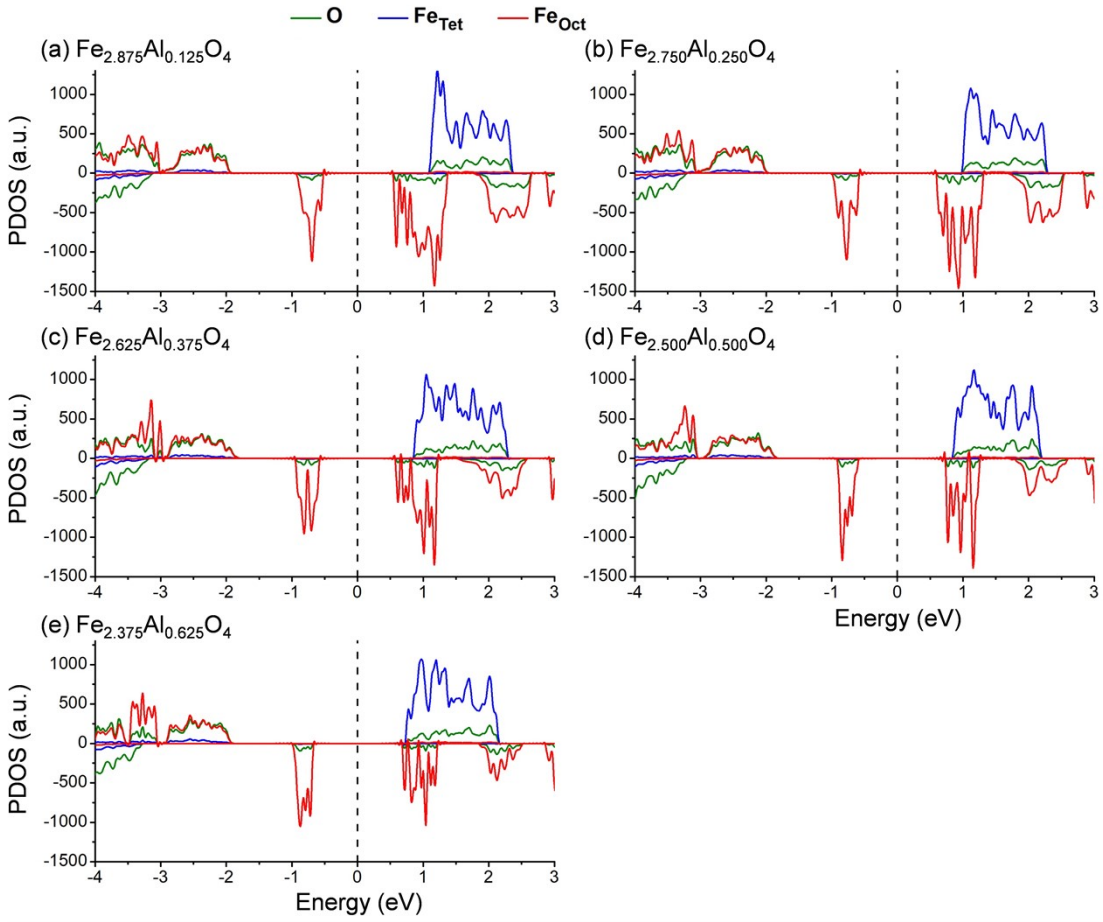

Figure S5. Projected density of states of Al-doped Fe_3O_4 at different Al concentration. The legend of colors is on the top. The Fermi level is scaled to zero as indicated by the dashed black lines.

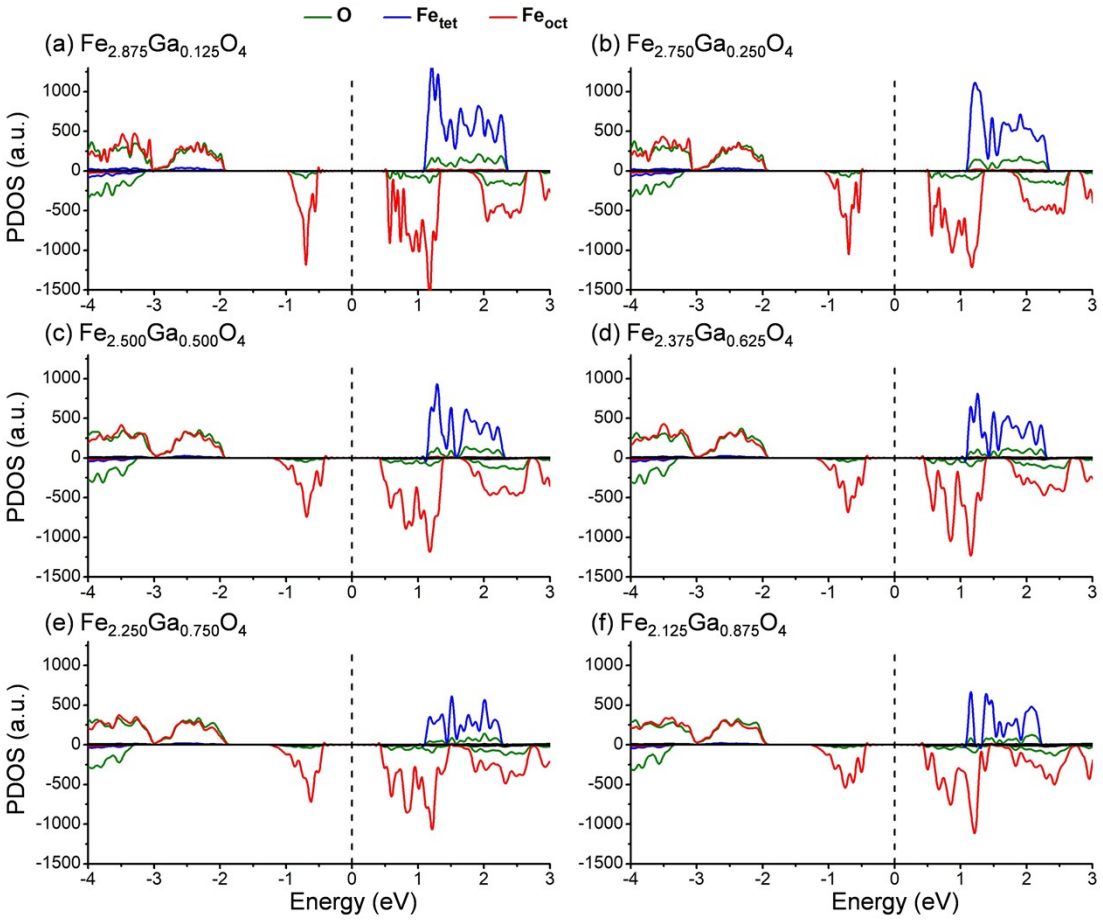

Figure S6. Projected density of states of Ga-doped Fe_3O_4 at different Ga concentration. The legend of colors is on the top. The Fermi level is scaled to zero as indicated by the dashed black lines.

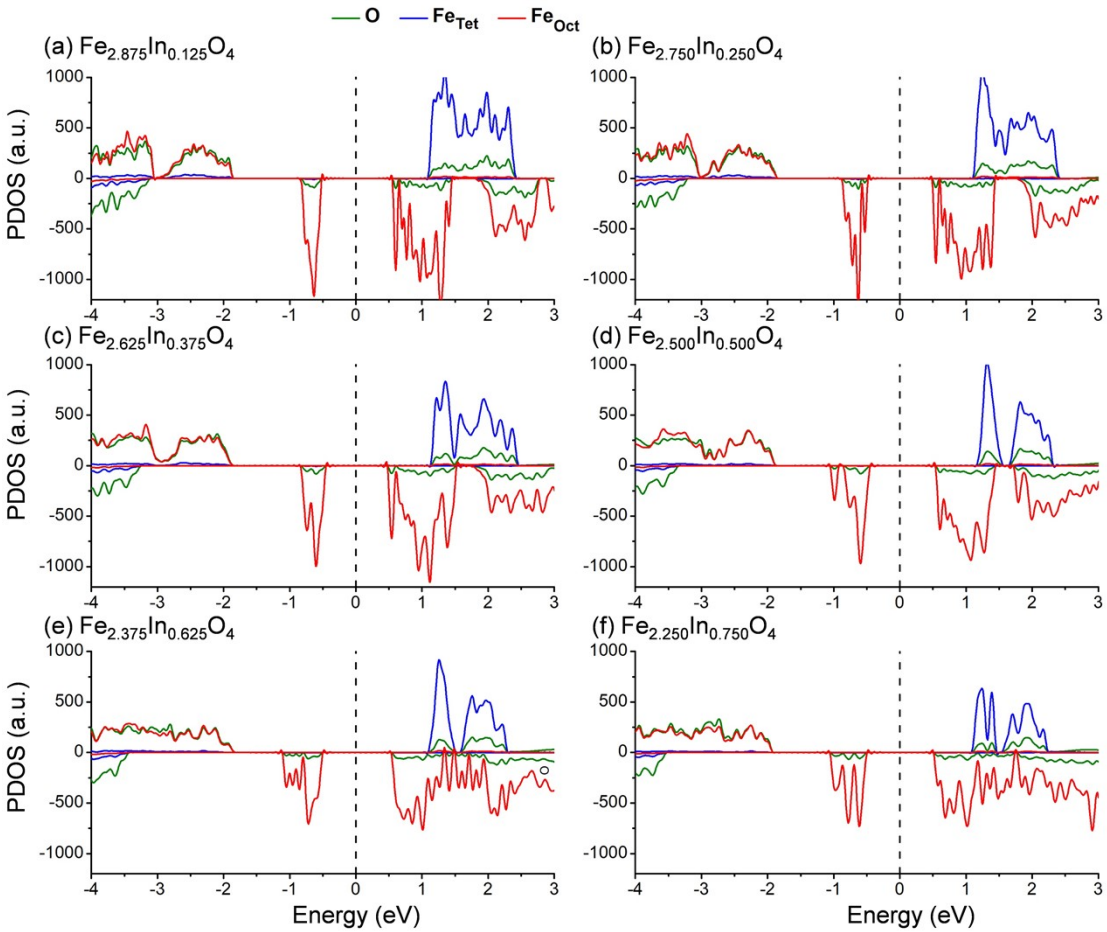

Figure S7. Projected density of states of In-doped Fe_3O_4 at different In concentration. The legend of colors is on the top. The Fermi level is scaled to zero as indicated by the dashed black lines.

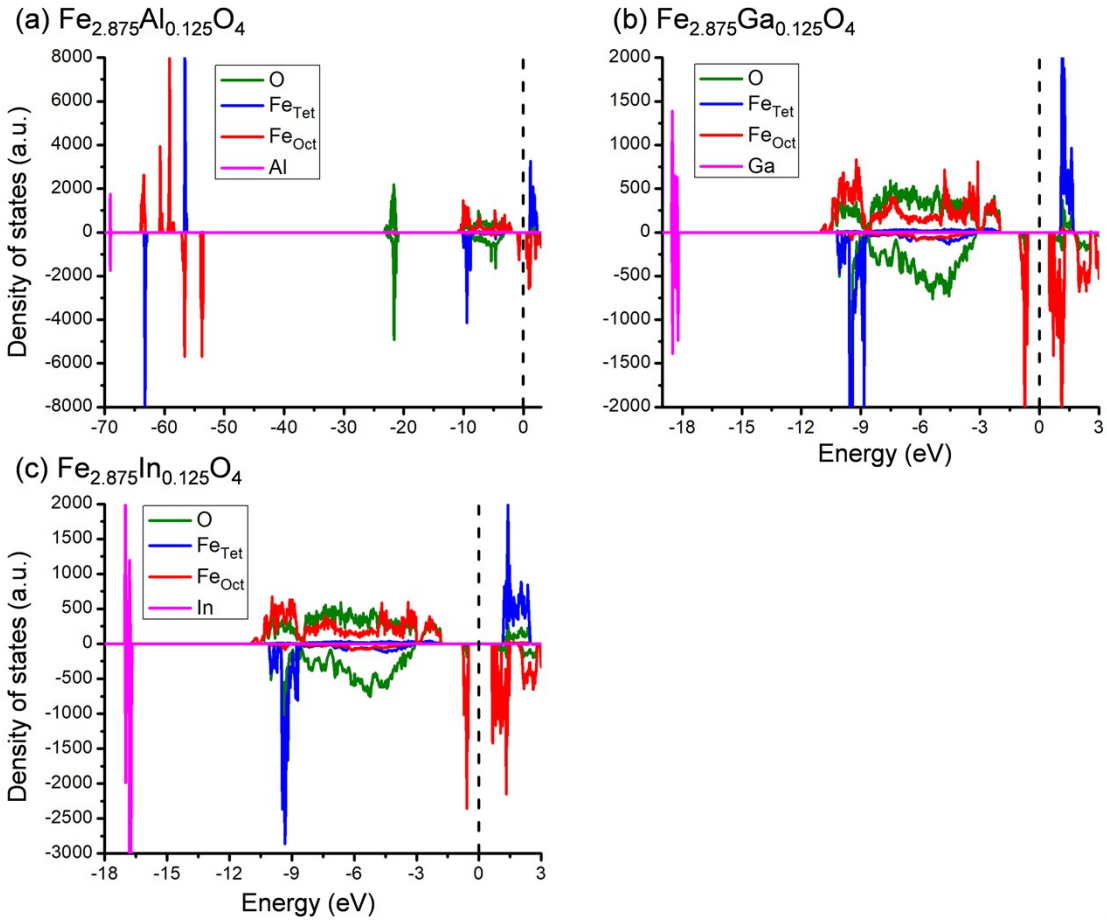

Figure S8. Projected density of states of (a) $Fe_{2.875}Al_{0.125}O_4$, (b) $Fe_{2.875}Ga_{0.125}O_4$ and (c) $Fe_{2.875}In_{0.125}O_4$ at a large range of energy. The Fermi level is scaled to zero as indicated by the dashed black lines.

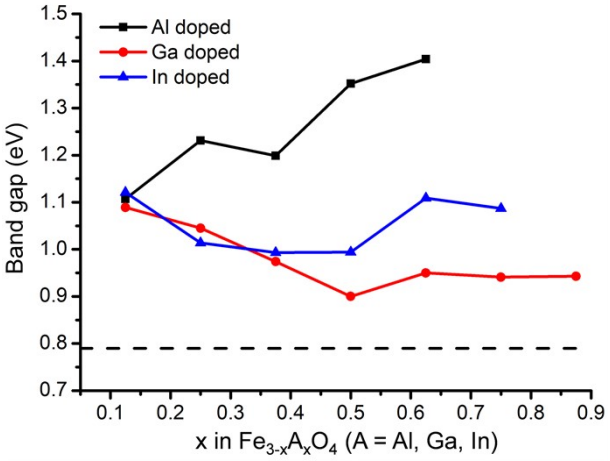

Figure S9. Band gap of Fe_3O_4 doped with group III elements (Al, Ga, In) as a function of doping concentration. The black dash line indicates the band gap value of Fe_3O_4 without doping.

Table S1. Relative energy for different configurations of $Fe_{2.125}Ga_{0.875}O_4$. The label Ga-mTnO (m and n are integers) means that m Ga atoms replace Fe_{Tet} and n Ga atoms replace Fe_{Oct}.

	Energy (eV)				
	Ga-7T	Ga-6T1O	Ga-5T2O	Ga-4T3O	Ga-7O
Fixed cell	0.000	-0.136	-0.146	0.052	0.759
Relaxed cell	0.000	-0.151	-0.170	-0.045	0.764