Understanding Hematite Doping with Group IV Elements: A DFT+U Study

Zhaohui Zhou,†‡ Pengju Huo,‡ Liejin Guo,‡ and Oleg V. Prezhdo*†‡

†International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Xi’an 710049, China
‡Department of Chemistry, University of Southern California, Los Angeles, California 90007, United States

Supporting Information

ABSTRACT: Si, Ge, or Sn doped hematite (α-Fe2O3) photoanodes show significantly enhanced efficiency for photo-oxidization of water. We employed DFT+U to study the doping of α-Fe2O3 with group IV elements, i.e., Si, Ge, and Sn. From the calculated formation energies and chemical potentials, three key points are concluded. (1) Low oxygen pressure is favored for doping both substitutional and interstitial dopants. (2) Substitutional doping of the Fe atom at the lattice site is more stable than interstitial doping in the octahedral vacancies. (3) Most interestingly, Ge doping is found to be easiest among the three dopants. This result contradicts intuition based on atomic size and indicates that Ge doping should be more efficient than Si and Sn doping in increasing the charge carrier concentration. Incorporation of the dopants at the Fe site generates an electron polaron and the dopant with the +4 valence state by spontaneous transfer of one electron from the dopant atom to a surrounding Fe atom, according to the analyses of charge transition energy levels and density of states. We identify the factors affecting the charge transfer process. The study elucidates the dopants role in increasing the electrical conductivity of α-Fe2O3 and provides guidelines for designing new efficient photoanodes.

1. INTRODUCTION

Photoelectrochemical (PEC) water splitting with semiconductors for sunlight harvesting has received extensive attention in recent years due to global energy and environment problems.1,2 Hematite (α-Fe2O3, hereafter Fe2O3) can absorb a large amount of sunlight with photon energy exceeding its band gap (~2.2 eV) and thus reach a 12.9% maximum theoretical photoconversion efficiency.3 In addition, Fe2O3 is inexpensive, nontoxic, abundant in the Earth’s crust, and inert to chemical corrosion in large pH ranges. These advantages make Fe2O3 a promising photoanode candidate with a state-of-the-art photoactivity.4 In order to understand the origin of improved PEC performance due to incorporation of group IV elements into Fe2O3 photoanodes, several calculations were performed. Liao et al. reported a simulation on electron transport in Ti, Zr, Si, and Ge doped Fe2O3 using cluster models at the unrestricted Hartree–Fock level.27 The main results were that Zr, Si, or Ge doping, superior to Ti doping, increased carrier concentration without impairing carrier mobility. A GGA+U study on Sn doped Fe2O3 reported by Meng et al.28 predicted that the improvement of PEC activity could be ascribed to the decreases in band gap and effective electron mass induced by Sn doping. The first-principles calculations at the level of hybrid density functional theory were also conducted on Si,23 Ge, and Sn29 doped Fe2O3 to interpret the improved photoactivity. For Si doping, the shrinking in the volume of the crystal cell was conjectured to facilitate hopping of localized charge carriers; for Ge and Sn doping, quite small band gaps of 0.2–0.3 eV were predicted due to creation of a donor state close to the conduction band minimum. Focusing on charge mobility and group IV elements, especially Si and Sn, were effective n-type dopants, modifying the optoelectronic properties of Fe2O3 electrodes for PEC applications.

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In n-type semiconductors, the electrical conductivity mainly depends on the electron carrier concentration and mobility. Here, we focus on the effect of doping on the electron concentration. Previously, the influence of doping on the electron mobility has been evaluated at low dopant concentration,\textsuperscript{27} which is typical in many experiments. We assess the ability of a dopant to increase the electron concentration by estimating its dopability. The dopability can be enhanced by good solubility and easy ionization of the dopant, while it is constrained by the compensation effect of native defects or defect complexes of the dopant.\textsuperscript{31,32} The dopant solubility determines the limits of dopant concentration, which depends exponentially on the formation energy.\textsuperscript{32,33} The dopant ionization depends on its charge transition energy level, which defines the Fermi level that leads to a new charge state. Thus, in this paper we study the solubility and ionization of group IV dopants by calculating the formation energy and charge transition energy levels using the DFT+U method. Densities of states are reported in order to establish the mechanism of internal charge transfer after incorporation of the Si, Ge, and Sn dopants into Fe$_2$O$_3$. In calculating the energy of formation, the chemical potentials of the elements are given close-packed lattice with 2/3 octahedral vacant sites occupied by Fe atoms.

We show that substitutional doping is more energetically favorable than interstitial doping due to different coordinations and orbital occupations of the two sites. Low oxygen pressure is favorable for doping. Contrary to intuition relying on atomic radii, Ge is more soluble in Fe$_2$O$_3$ than Si and Sn due to balance between atomic radius and enthalpy of formation. Analysis of the formation energies rationalizes the thermal activation phenomena observed in many Fe$_2$O$_3$ photoanodes. The doping leads to formation of electron polaron as a result of electron transfer from the dopant atom to a surrounding Fe atom. The spontaneous dopant ionization leads to the +4 valence state. The established doping and charge transfer rules provide guidelines for increasing efficiencies of photoelectrode materials.

2. COMPUTATIONAL DETAILS

2.1. Computational Models and Setup. The geometry and magnetization of the crystallographic hexagonal cell for Fe$_2$O$_3$ are shown in Figure 1. O atoms form the hexagonal close-packed lattice with 2/3 octahedral vacant sites occupied by Fe atoms. Pure Fe$_2$O$_3$ has an antiferromagnetic ground state with Fe atoms in the buckled plane coupled ferromagnetically with each other and Fe atoms in adjacent planes coupled antiferromagnetically. In order to simulate doping effects, the 2 × 2 × 1 supercell was employed. A 3 × 3 × 1 supercell was used to check convergence of the formation energy and charge transition energy level with respect to the supercell size. For substitutional dopants (X), one of the 4 (9) iron atoms labeled as Fe4 (see Figure 1) in the 2 × 2 × 1 (3 × 3 × 1) supercell was replaced by one of the group IV atoms. For interstitial dopants (X'), one of the 4 (9) remaining octahedral vacancies within the Fe2–Fe3 buckled plane was occupied with one of the group IV atoms.

The first-principles calculations on X doped Fe$_2$O$_3$ (X:Fe$_2$O$_3$) were performed within the framework of spin-polarized density functional theory with the on-site Coulomb correction (DFT+U).\textsuperscript{34} As implemented in the VASP code.\textsuperscript{35,36} The exchange-correlation functional was treated within the generalized gradient approximation (GGA) with the formalism of Perdew–Burke–Ernzerhof (PBE).\textsuperscript{37} The strongly correlated electronic nature in Fe$_2$O$_3$ was treated by the Coulomb correction (U = 5 eV and J = 1 eV) solely on Fe 3d electrons. The projector augmented wave (PAW) potential was employed to describe the electron–ion interaction.\textsuperscript{38} The plane-wave basis set with the energy cutoff of 520 eV was used to expand the electronic wave function. The Monkhorst–Pack k-point grid\textsuperscript{39} of 3 × 3 × 3 was adopted to sample the Brillouin zone of the 2 × 2 × 1 supercell, and the grid of 1 × 1 × 1 was used for the 3 × 3 × 1 supercell. The valence electron configurations were O 2s$^2$2p$^4$, Fe 3d$^7$4s$^2$, Si 3s$^2$3p$^2$, Ge 3d$^{10}$4s$^2$4p$^2$, and Sn 4d$^{10}$5s$^2$5p$^2$. Semicore 3p electrons of Fe atom were not treated as valence electrons in the current calculations because the effect of 3p electrons on the ground state properties was negligible.\textsuperscript{40}

The geometry optimization of the crystallographic hexagonal cell for pure Fe$_2$O$_3$ was performed at the PBE and PBE+U levels. Structural parameters and band gap are summarized in Table 1. The PBE+U calculation produced a crystal structure which was similar to the structure obtained from the PBE calculation. At the same time, PBE+U significantly improved the band gap, which was consistent with previous studies.\textsuperscript{40,41}

![Figure 1. Crystallographic hexagonal cell for Fe$_2$O$_3$ with directions of magnetic moment on Fe atoms labeled. Small red and big brown balls represent O and Fe atoms, respectively.](image)

### Table 1. Lattice Constants (a and c), Fe–O Bond Lengths, and Band Gap of Pure Fe$_2$O$_3$ Computed with PBE and PBE + U and the Corresponding Experimental Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PBE</th>
<th>PBE+U</th>
<th>Expt$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.008</td>
<td>5.071</td>
<td>5.035</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.870</td>
<td>13.903</td>
<td>13.747</td>
</tr>
<tr>
<td>Fe–O bond (Å)</td>
<td>1.926 × 3</td>
<td>1.966 × 3</td>
<td>1.945 × 3</td>
</tr>
<tr>
<td>2.136 × 3</td>
<td>2.122 × 3</td>
<td>2.113 × 3</td>
<td></td>
</tr>
<tr>
<td>band gap (eV)</td>
<td>0.52</td>
<td>2.15</td>
<td>2.0–2.2$^b$</td>
</tr>
</tbody>
</table>

$^a$Structural parameters from ref 42. $^b$Optical band gaps from ref 40.
2.2. Energy of Formation. The energy of formation for dopant X in charge state $q$ in Fe$_2$O$_3$ is defined as

$$E^q(X) = E^q(\text{Fe}_2\text{O}_3) - E(\text{Fe}_2\text{O}_3) + n_q \mu_q - \mu_X + q(e_F + E_{\text{VBM}} + \Delta V)$$

(1)

$E(\text{Fe}_2\text{O}_3)$ is the total energy of pure Fe$_2$O$_3$, and $E^q(\text{Fe}_2\text{O}_3)$ is the total energy of the supercell with one dopant in charge state $q$. When $E^q(\text{Fe}_2\text{O}_3)$ was calculated, $q$ electrons were removed (added) from (to) the supercell to achieve the positive (negative) value of $q$. $\mu_q$ and $\mu_X$ denote the respective chemical potentials of X elements. $n_q$ is the number of Fe atoms removed from the supercell of pure Fe$_2$O$_3$; $n_q = 1$ or 0 for substitutional or interstitial doping. $e_F$ is the Fermi level, with respect to the valence band maximum $E_{\text{VBM}}$ of pure Fe$_2$O$_3$.

For charged supercells, the energy converges very slowly with respect to the supercell size. Thus, two correction terms were taken into consideration when calculating the energy of formation for charged systems. The first term is the potential alignment correction which aligns the electrostatic potential in the doped supercell with that of pure Fe$_2$O$_3$ by adding a constant shift $\Delta V$. $\Delta V$ was estimated by comparing the electrostatic potential at the O core in the bulk-like region in the supercell containing one neutral dopant with that in pure Fe$_2$O$_3$. Another term is caused by the Coulomb interaction between the charged dopant and its images due to periodic boundary conditions. The leading error was corrected by the first-order correction proposed by Makov and Payne with a static dielectric constant of 22.9. The combination of these two terms has been validated to be effective to correct the formation energy of a charged system. The calculated values of the two terms are presented in Table S1 of the Supporting Information.

The charge transition energy level $\epsilon(q/q')$ is defined as the Fermi level $e_F$ in eq 1 at which the energies of formation for dopant X in charge states $q$ and $q'$ are equal, i.e.

$$\epsilon(q/q') = ([E^q(\text{Fe}_2\text{O}_3) - E^q(\text{Fe}_2\text{O}_3)]/(q' - q) - (E_{\text{VBM}} + \Delta V)$$

(2)

Here $\epsilon(q/q')$ is defined relative to the valence band maximum of doped Fe$_2$O$_3$. The function $\epsilon(q/q')$ allows us to judge the feasibility of dopant ionization and to determine the dopant stability in different charge states. For example, $\epsilon(+1/0)$ is the Fermi level, below which the +1 charge state is more stable than the 0 charge state and above which the opposite holds.

3. RESULTS AND DISCUSSION

3.1. Chemical Potentials. The energies of formation in eq 1 for group IV dopants in Fe$_2$O$_3$ were dependent on the chemical potentials of Fe and dopant elements, i.e., $\mu_{Fe}$ and $\mu_X$. Thus, the allowed ranges of $\mu_{Fe}$ and $\mu_X$ had to be determined first.

For pure Fe$_2$O$_3$ in thermodynamic equilibrium, the chemical potentials of Fe and O elements should satisfy

$$2\mu_{Fe} + 3\mu_{O} = E(\text{Fe}_2\text{O}_3)$$

(3)

Equation 3 has another form in which the formation enthalpy of Fe$_2$O$_3$ is employed. This form was not adopted because the calculation of the formation enthalpy is problematic within the DFT+$U$ framework.

To avoid precipitation of elemental Fe and dopant X, and generation of gaseous O$_2$, these chemical potentials are restricted by

$$\mu_{Fe} \leq E(\text{Fe}), \quad \mu_X \leq E(X), \quad \mu_{O} \leq \frac{1}{2}E(\text{O}_2)$$

(4)

Meanwhile, to avoid formation of secondary phases between dopants and oxygen, $\mu_{O}$ is also limited by

$$\mu_{O} + 2\mu_{X} \leq E(\text{XO}_3)$$

(5)

Therefore, $\mu_{O}$ in the O-rich limit is half of the total energy of the O$_2$ molecule, according to the last inequality in eq 4, and the corresponding $\mu_{Fe}$ and $\mu_X$ could be obtained according to eqs 3 and 5, respectively. Because of the overbinding in O$_2$ molecules within the GGA approximation, an overestimated binding energy of 6.04 eV was obtained with the PBE calculation. To correct this overbinding, the experimental binding energy of 5.23 eV was used to derive the total energy of the O$_2$ molecule.

On the other hand, $\mu_{O}$ in the Fe-rich limit was determined, as proposed by Lee et al., by considering the phase transition from Fe$_2$O$_3$ to Fe$_3$O$_4$ as the oxygen pressure decreased, i.e.

$$\mu_{O}^{\text{Fe-rich}} = 3E(\text{Fe}_2\text{O}_3) - 2E(\text{Fe}_3\text{O}_4)$$

(6)

The ambient phase Fe$_3$O$_4$ with a cubic inverse spinel structure was adopted here, and the same value of $U$ was applied on Fe 3d electrons as for Fe$_3$O$_4$. Then, the corresponding $\mu_{Fe}$ and $\mu_X$ in the Fe-rich limit were obtained as in the O-rich limit. As-derived chemical potentials are summarized in Table 2, and the allowed ranges of the chemical potentials for the Fe and Si elements in Si doped Fe$_2$O$_3$ are pictured in Figure 2, as functions of $\mu_{Fe}$ and $\mu_{Si}$.

Table 2. Calculated Chemical Potentials ($\mu$, in eV) of O, Fe, Si, Ge, and Sn Elements at O-Rich and Fe-Rich Conditions

<table>
<thead>
<tr>
<th>Element</th>
<th>O-Rich</th>
<th>Fe-Rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{O}$</td>
<td>-4.52</td>
<td>-10.44</td>
</tr>
<tr>
<td>$\mu_{Si}$</td>
<td>-14.67</td>
<td>-10.33</td>
</tr>
<tr>
<td>$\mu_{Ge}$</td>
<td>-14.67</td>
<td>-10.33</td>
</tr>
<tr>
<td>$\mu_{Sn}$</td>
<td>-14.67</td>
<td>-10.33</td>
</tr>
</tbody>
</table>

To justify feasibility of the method, $\mu_{Fe}$ in the Fe-rich limit derived above should be compared with that from the first inequality in eq 4, and similarly, $\mu_{X}$ in the Fe-rich limit should
also be compared with that from the second inequality in eq 4. The calculated total energies at the PBE level for the Si, Ge, and Sn elementary crystals were \(-5.42, -4.62,\) and \(-4.01\) eV/atom, respectively, and the total energy for the Fe crystal at the PBE+U level \((U = 5\) eV) was \(-5.33\) eV/atom, indicating that reasonable chemical potentials of these elements in the Fe-rich limit could be taken from eqs 5 and 6.

### 3.2. Energy of Formation

The enthalpies of formation for \(\text{Fe}_2\text{O}_3\), \(\text{Fe}_3\text{O}_4\), \(\text{SiO}_2\), \(\text{GeO}_2\), and \(\text{SnO}_2\) were calculated at the PBE level and compared with the corresponding experimental values, as summarized in Table 3. It could be found that for SiO\(_2\), GeO\(_2\), and SnO\(_2\), the agreement between calculations and experimental values at the ground state \(\left(0\text{ K, }0\text{ MPa}\right)\) was poor, probably due to their strongly correlated electronic structure. The chemical potentials taken from eqs 5 and 6, which indicated that taking secondary oxides, and application of eq 3 was required due to the imperfect enthalpy of formation calculated for \(\text{Fe}_2\text{O}_3\). The energies of formation for the neutral \(\text{X}_s\) and \(\text{X}_i\) dopants in \(\text{Fe}_2\text{O}_3\) were calculated according to eq 1 and are summarized in Table 4. First of all, the \(2 \times 2 \times 1\) supercell was verified to be sufficient for most of the dopants to obtain well-converged energies of formation except for the interstitial Si dopant where the energy of formation was increased by 0.23 eV when the \(3 \times 3 \times 1\) supercell was used. Next, energies of formation decreased significantly under the Fe-rich condition, indicating that low oxygen pressure is favorable for incorporation of the group IV dopants. Third, \(E'_f(X_i)'s\) were found to be much lower than \(E'_f(X_s)'s\) under both O-rich and F-rich conditions, indicating that \(X_i\) was more stable than \(X_s\) in Fe\(_2\)O\(_3\). This result was consistent with that reported by Liao et al., who showed that the substitutional doping of Si and Ge dopants is favored with respect to the interstitial doping in the tetrahedral coordination. Note that our results are obtained with larger unit cells and for octahedral interstitial sites. The higher stability for the \(X_i\) dopants could be ascribed to the stronger interaction between the dopant and its surrounding O atoms, which was induced by the difference in the coordination of the \(X_i\) and \(X_s\) dopants. The effect is discussed further in section 3.4.

<table>
<thead>
<tr>
<th>X</th>
<th>Si:Fe(_2)O(_3)</th>
<th>Ge:Fe(_2)O(_3)</th>
<th>Sn:Fe(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X_s) O-rich</td>
<td>2.41 (2.40)</td>
<td>1.45 (1.46)</td>
<td>1.81 (1.80)</td>
</tr>
<tr>
<td>Fe-rich</td>
<td>1.08 (1.07)</td>
<td>0.12 (0.12)</td>
<td>0.48 (0.47)</td>
</tr>
<tr>
<td>(X_i) O-rich</td>
<td>7.41 (7.64)</td>
<td>7.02 (7.02)</td>
<td>8.06 (8.05)</td>
</tr>
<tr>
<td>Fe-rich</td>
<td>2.09 (2.32)</td>
<td>1.70 (1.70)</td>
<td>2.74 (2.73)</td>
</tr>
</tbody>
</table>

The highest photocurrent density reported for Ge doped \(\text{Fe}_2\text{O}_3\) was smaller than those for Si and Sn doped \(\text{Fe}_2\text{O}_3\), i.e., 1.4, 1.86, and 2.2 mA/cm\(^2\) at 1.23 V vs reversible hydrogen electrode at the standard measuring conditions for Ge, Sn, and Si doped \(\text{Fe}_2\text{O}_3\), respectively. It has been reported that an annealing process is often required to activate many \(\text{Fe}_2\text{O}_3\) photoanodes, such as Ti\(_{30,51}\), Ge\(_{26}\), and Sn\(_{13}\) doped \(\text{Fe}_2\text{O}_3\), fabricated with various solution-based methods. The annealing process not only makes \(\text{Fe}_2\text{O}_3\) recrystallize at a high temperature and thus reduces defects in the crystal but also activates the dopants incorporated into \(\text{Fe}_2\text{O}_3\). The performance of water photo-oxidation conducted on Ge and Sn doped \(\text{Fe}_2\text{O}_3\) electrodes was compared, and the optimal temperature (550 °C) for Ge doped \(\text{Fe}_2\text{O}_3\) was found to be substantially lower than that (800 °C) for Sn doped \(\text{Fe}_2\text{O}_3\), while their optimal efficiencies were comparable. Although the high temperature needed for activation of
Sn doped Fe$_2$O$_3$ may be in part attributed to the slow diffusion of large Sn ions from the electrode, it is an indication that the activation process is easier for Ge atom than Sn atom in Fe$_2$O$_3$. The result is consistent with the calculated formation energies. As for Si doped Fe$_2$O$_3$, most of the systems are fabricated using ultrasonic spray pyrolysis$^{15,35}$ or atmospheric pressure chemical vapor deposition (APCVD).$^{7,8,10,23}$ These approaches involve nonequilibrium processes, which are beyond the scope of this paper. The typical temperatures between 400 and 500 °C are even lower than those for Ge doped Fe$_2$O$_3$ because the chemical potential of Si may be increased out of the thermodynamics equilibrium range due to the nonequilibrium processes. This hypothesis can be supported by the formation of elementary Si in Si doped Fe$_2$O$_3$ (APCVD), identified by X-ray photoelectron spectroscopy.$^{25}$ If the chemical potential of Si is taken from the elementary crystal, we obtained dramatically reduced formation energy that makes the activation of Si dopant much easier.

3.3 Charge Transition Energy Levels. The charge transition energy levels for Xs doped Fe$_2$O$_3$ were calculated according to eq 2 and plotted in Figure 3. The charge transition levels were checked with respect to the supercell size and found to be converged within 0.1 eV when the 2 × 2 × 1 supercell was used. $\epsilon$(+1/0)’s for Xs doped Fe$_2$O$_3$ were well within the band gap and consistent with the charge transition level for the electron polaron at 1.77 eV reported by Lee et al.$^{33}$ indicating that the electron polaron might be formed in these doped Fe$_2$O$_3$ due to the spontaneous donation of one electron from the Xs dopant to a surrounding Fe atom. The $\epsilon$(+2/+1) values were estimated to reside below the valence band maximum and also below the delocalized hole at −0.06 eV, which was calculated by removing one electron from pure Fe$_2$O$_3$. The $\epsilon$(+3/+2) and $\epsilon$(+4/+3) levels are expected below $\epsilon$(+2/+1) and also within the valence bands. They should correspond to the ionization of the other two electrons in the chemical bond. Because these levels are far away from the band gap, and since the high charge states will induce stronger spurious Coulomb interaction between the dopant and its images, the $\epsilon$(+3/2) and $\epsilon$(+4/3) levels are not calculated here. Thus, the stable charge states for the Xs doped Fe$_2$O$_3$ were 0 with the electron polaron created, or +1 with the electron polaron ionized to compensate for the intrinsic defects, for example the Fe vacancy.$^{33}$ When the Fermi level was within the band gap, the dopants Xs should be capable of being spontaneously ionized to create the electron polaron with the Fermi level in the band gap. From this point of view, the group IV dopants are superior to the intrinsic Fe interstitial which was estimated to be the main source for the n-type conduction in intrinsic Fe$_2$O$_3$.$^{33}$

3.4 Density of States. In order to investigate the possible charge transfer occurring in Xs doped Fe$_2$O$_3$, the calculated density of states is presented in Figures 4 and 5. It could be observed from Figures 4a, 5a, and 5b that an impurity state occurred in the band gap of the spin-up channel and that, meanwhile, some states were created just above the valence band maximum in the spin-down channel. By projecting on the atoms of each species, we established that the occupied impurity states were dictated by the contribution from Fe atoms rather than the dopant atoms. Further analysis indicated that the Fe atom related to the impurity states was one of the four Fe3 atoms which were just below the dopant atom, as shown in Figure 4b. A dopant atom has 4 valence electrons, and 3 of them would be formally transferred to the O atoms after the dopant was bonded with the surrounding O atoms. The excess electron could be donated to one of the surrounding Fe atoms, here a Fe3 atom, which have high energy levels. The electron transfer results in formation of an electron polaron and an ionized dopant with the +4 valence state, as anticipated in section 3.3. The favorable substitutional dopants with the +4 valence state agree with several experimental observations. Cesar et al. investigated the influence of film thickness, feature size, and Si doping on the performance of nanostructured Fe$_2$O$_3$ photoanodes and indicated the lattice substitution of Fe$^{3+}$ by Si$^{4+}$. The substitution of Fe by Si in Si doped Fe$_2$O$_3$ nanosheets with superlattice structure synthesized by Liu et al. was confirmed by micro-Raman spectra.$^{33}$ Liu et al. also reported the substitution of Ge$^{4+}$ at Fe$^{3+}$ sites in Fe$_2$O$_3$ nanosheets by combining the XPS and XRD analyses.$^{19}$ Ling et al. reported nanowires and nanocorals of Sn doped Fe$_2$O$_3$ photoanodes and indicated the lattice substitution of Sn$^{4+}$ at Fe$^{3+}$ sites by the XPS analysis.$^{16}$ The band structures for Si, Ge, and Sn doped Fe$_2$O$_3$ are presented in Figure S1 of the Supporting Information.

Figure 4. (a) Total and projected densities of states for the Si, O, and Fe atoms in Fe$_2$O$_3$ and (b) projected density of states on the Fe atoms in the vicinity of the Si atom. The density of states projected on the Si atom was magnified 10 times for easy visualization.
localized state in the middle of the band gap and localized states just above the valence band maximum were observed in all three cases. These results are consistent with the density of states data. The small dispersion of the impurity states illustrates the poor mobility of electron polarons, which is intrinsic for electron polarons in Fe$_2$O$_3$.

Three points could be summarized about the charge transfer in doped Fe$_2$O$_3$. First, the excess electron on the dopant atom was transferred to an adjacent layer of Fe atoms which possessed an opposite magnetic moment, just as in Ti doped Fe$_2$O$_3$\textsuperscript{54}, although the dopant itself did not possess any magnetic moment. Second, the excess electron was transferred to the Fe atom layer below the dopant, i.e., one Fe$_3$ atom instead of one Fe6 or Fe7 atom (see Figure 1). The reason could be ascribed to the difference in the length of the X(Fe4)–O bond above and below the dopant (the bonds above the Fe4 atom were longer than those below, as shown in Table 1).

The last point concerned the Fe3 atom to which the excess electron was transferred in the current models, i.e., the relation between the electron transfer and internal geometry structure. An electron was transferred from Si, Ge, and Sn dopants to different Fe3 atoms. For example, the electron was transferred to Fe3(O1) in Si doped Fe$_2$O$_3$, Fe3(O3) in Ge doped Fe$_2$O$_3$, and Fe3(O2) in Sn doped Fe$_2$O$_3$ (see Figure 6 for notation). From the X–O and Fe3–O bonds listed in Figure 6, it could be

![Figure 5](https://example.com/image5.png)

**Figure 5.** Total and projected densities of states of the dopant, O, and Fe atoms for (a) Ge, (b) Sn, and (c) Si, doped Fe$_2$O$_3$. The densities of states projected on the dopant atoms were magnified 10 times for easy visualization.

![Figure 6](https://example.com/image6.png)

**Figure 6.** Local atomic structure in Fe$_2$O$_3$ around the dopants with the length of X–O (X = Si, Ge, and Sn) and Fe3–O bonds listed. Fe3(O1/O2/O3) denotes the Fe3 atom immediately connected with the O1, O2, or O3.

found that once the electron on the dopant was donated to one Fe3 atom, the X–O bond with the O atom immediately connected to the Fe3 atom was the shortest and the corresponding Fe3–O bond was the longest. The expanded Fe3–O bond suggested that the valence state of the Fe3 atom formally changed from +3 to +2, as in the electron polaron model.

In addition, three types of possible optical absorption were classified for X$_i$ doped Fe$_2$O$_3$ from the corresponding density of states. The intrinsic absorption wavelength was estimated to be around 650 nm for X$_i$ doped Fe$_2$O$_3$, which was slightly longer than the experimental values\textsuperscript{13,23,26,52}. The signal is caused by the transition from the valence band to the conduction band in the spin-up channel. The next type of absorption with a wavelength around 770 nm was ascribed to the transition from the impurity states above the valence band to the conduction band in the spin-down channel. The absorption wavelength was in coincidence with the experimentally reported values around 750 nm\textsuperscript{13,26,52}. The absorption starting from 1250 nm was due to the transition from the impurity state in the middle of band gap to the conduction band in the spin-up channel. This type of absorption was not measured in the experiments, possibly because the excitation energy is insufficient for water splitting, and therefore it is of little practical interest.

In the end, the reason for different stabilities of X$_i$ and X$_s$ dopants in Fe$_2$O$_3$ was discussed, as indicated by the calculated energies of formation, from the viewpoint of orbital occupations. For X$_i$ dopants, only one excess electron was left after the other three electrons were transferred to the nearest O atoms; hence, only one electron was donated to four empty Fe d orbitals, as shown in Figure 4. For X$_s$ dopants, however, all four electrons were left because all O atoms in Fe$_2$O$_3$ were saturated. These electrons could merely be donated to four empty Fe d orbitals, and thus four impurity states were created in the band gap with two states in each spin channel, as shown in Figure 5c. Although more electron polarons were generated due to more occupied Fe d orbitals in X$_s$ doped Fe$_2$O$_3$, from the X–O and Fe3–O bonds listed in Figure 6, it could be
Fe$_x$O$_y$, the system also became more unstable because the occupied Fe d orbitals are higher in energy than the bonding orbitals of X–O, as suggested by the charge transition levels $\varepsilon^{(+2/+1)}$ below the valence band maximum.

4. CONCLUSIONS

In summary, we conducted the DFT+U calculations to study the doping of group IV elements (X = Si, Ge, and Sn) into Fe$_x$O$_y$. From the calculated energies of formation, we have found that low oxygen pressure is a favorable factor for incorporation of the group IV substitutional and interstitial dopants into Fe$_x$O$_y$. Furthermore, the substitutional doping is favored with respect to the interstitial doping, and the reason can be ascribed to the saturated coordination of the interstitial dopants and the unavoidable occupation of more Fe d orbitals. Most intriguingly, we found Ge has the highest solubility among the three dopants. The reason can be attributed to the intermediate Ge atomic radius and the small formation enthalpy of secondary phase GeO$_2$. The result is rather unexpected, since it goes counter to intuition based purely on atomic size. The calculated formation energies rationalize the thermal activation phenomena observed in many Fe$_x$O$_y$ photoanodes. Further analyses of charge transition energy levels and densities of states have indicated that an electron polaron and the dopant with the +4 valence state are generated simultaneously due to the electron transfer from the dopant atom to a surrounding Fe atom. The rules of charge transfer were also elucidated. The reported results are particularly valuable for design of novel photoanodes based on Fe$_x$O$_y$ and related materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b08081.

Band dispersions for Si, Ge, and Sn doped Fe$_x$O$_y$ (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: prezhd@usc.edu (O.V.P.).

Notes

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