Co-Substituted BiFeO$_3$: Electronic, Ferroelectric, and Thermodynamic Properties from First Principles

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Bismuth ferrite, BiFeO$_3$, is a multiferroic solid that is attracting increasing attention as a potential photocatalytic material, because the ferroelectric polarization enhances the separation of photogenerated carriers. With the motivation of finding routes to engineer the band gap and the band alignment, while conserving or enhancing the ferroelectric properties, the thermodynamic, electronic, and ferroelectric properties of BiCo$_x$Fe$_{1-x}$O$_3$ solid solutions ($x = 0$, 0.0625, 0.125) using density functional theory are investigated. It is shown that the band gap can be reduced from 2.9 to 2.1 eV by cobalt substitution, while simultaneously increasing the spontaneous polarization, which is associated with a notably larger Born effective charge of Co compared to Fe cations. The interaction between Co impurities is discussed, which is strongly attractive and can drive the aggregation of Co, as evidenced by Monte Carlo simulations. Phase separation into a Co-rich phase is therefore predicted to be thermodynamically preferred, and the homogenous solid solution can only exist in metastable form, protected by slow cation diffusion kinetics. Finally, the band alignment of pure and Co-substituted BiFeO$_3$ with relevant redox potentials, in the context of its applicability in photocatalysis, is discussed.

1. Introduction

Multiferroic materials, which simultaneously exhibit two or more ferroic properties (ferromagnetism or antiferromagnetism, ferroelectricity, and ferroelasticity), are promising for a range of functional applications.[1] Bismuth ferrite (BiFeO$_3$) is among the few attractive multiferroic materials with both ferroelectric and (anti)ferromagnetic behavior at room temperature. It has a high ferroelectric-to-paraelectric transition point (Curie temperature $T_C = 1103$ K) and an antiferromagnetic-to-paramagnetic transition point also well above ambient temperature (Néel temperature $T_N = 643$ K).[2] The crystal structure (Figure 1) of BiFeO$_3$ at ambient conditions is rhombohedral (space group $R$3$_c$), with lattice parameter $a = 5.64$ Å and rhombohedral angle $\alpha = 59.4^\circ$. The off-center displacements of the Fe and O atoms with respect to the Bi sub-lattice result in a large spontaneous polarization along the pseudo-cubic [111] direction, primarily due to Bi translation along this direction.[6,7] The structure is also piezoelectric at all temperatures below $T_C$. Its magnetic structure below $T_N$ is, in a first approximation, G-type antiferromagnetic, which means that each Fe$^{3+}$ spin is surrounded by antiparallel spins on nearest-neighbor Fe sites, leading to zero net moment; however, there is actually a weak net magnetic moment per unit cell, which results from spin canting due to the symmetry breaking induced by the ferroelectric polarization.[8] These properties make BiFeO$_3$ a promising room-temperature single-phase multiferroic material, with potential applications in data storage, spin valves, spintronics, and sensors.[2]

Recently, there has also been increasing interest in using BiFeO$_3$ for photovoltaic[10–15] and photocatalytic[16–26] applications. This attention is motivated by the ferroelectric character of this oxide, because its internal electric field can be exploited to aid the separation of oppositely charged photogenerated carriers and/or to engineer the band alignment. Furthermore, BiFeO$_3$ has a relatively narrow band gap (most commonly reported values for thin films range between 2.6 and 2.8 eV)[27] compared to other ferroelectric oxides, which makes it especially attractive for optical applications. Since this band gap is still somewhat too wide for optimal visible light absorption, there have been efforts to use chemical substitutions to make it narrower, while retaining or improving the ferroelectric properties of the oxide. Peng et al.[28] showed that Co/Fe substitution led to narrower band gaps (e.g., from 2.66 eV in pure BiFeO$_3$ to 2.53 eV in BiCo$_{0.4}$Fe$_{0.6}$O$_3$). Recent experimental work by Machado et al.[13,14] has shown that,
in addition to decreasing the band gap, Co/Fe substitutions can increase the spontaneous polarization of BiFeO$_3$, which might be a bonus for photovoltaic and photocatalytic applications, by enhancing carrier separation.

We are particularly interested here in the applications of BiFeO$_3$ and BiCo$_x$Fe$_{1-x}$O$_3$ in photocatalysis. Despite having an adequate band gap, there is evidence that pure BiFeO$_3$ does not have the right band alignment for the full water splitting reaction and therefore is inactive as a single-semiconductor photocatalyst for that reaction.$^{[25]}$ but it can still be used for water photo-oxidation biased by sacrificial agents (which are then reduced instead of the protons).$^{[29]}$ BiFeO$_3$ also shows promising behavior when used as part of heterojunctions for water-splitting photocatalysis. For example, CdS/BiFeO$_3$ heterojunctions forming a Z-scheme have been found to be active as particulate photocatalysts for water splitting without using any sacrificial agents.$^{[25]}$ Furthermore, BiFeO$_3$-based materials can be used as photoanodes in tandem photoelectrochemical (PEC) cells, where the photoanode or photocathode only need to have suitable band alignment for one half-reaction. Khoomortezai et al. have demonstrated that photoanodes made of WO$_3$/BiVO$_4$/BiFeO$_3$$^{[22]}$ or WO$_3$/BiFeO$_3$$^{[24]}$ heterojunctions are efficient in photo-electrochemical water splitting. BiFeO$_3$ can also be useful as photocatalyst (or part of them) for other reactions, such as the degradation of organic pollutants (see ref. [19] for a review). For example, studies involving both pure$^{[17]}$ and doped$^{[21]}$ BiFeO$_3$, as well as BiFeO$_3$-containing heterojunctions (e.g., with C$_3$N$_4$)$^{[20]}$ have shown that BiFeO$_3$ is an active photocatalyst for degrading rhodamine B, an organic dye that is widely used as a colorant in the textile industry, and can be toxic to humans and animals if not removed from wastewaters. Mushkaq et al. have shown that the photocatalytic activity of BiFeO$_3$ in the degradation of rhodamine B can be enhanced under mechanical vibrations thanks to piezo-photocatalytic effects.$^{[21]}$ In these applications, the ferroelectric character of BiFeO$_3$ is beneficial to the photocatalytic process by aiding the separation of photogenerated carriers. Recent work by Huang et al.$^{[26]}$ has shown that the effect can be enhanced by electrically poling (via the application of an external electric field) the BiFeO$_3$ nanoparticles to align the ferroelectric domains, which accelerated the photocatalytic process by a factor of two compared with unpoled BiFeO$_3$. There is also evidence that the orientation of the ferroelectric polarization can be used to engineer photocatalytic response.$^{[18,30]}$ The interplay between ferroelectric and photocatalytic properties in this material clearly deserves further research attention at the theoretical level to improve our fundamental understanding of these phenomena, which will help rationalizing the design of better BiFeO$_3$-based photocatalysts.

In this work, we use density functional theory (DFT) simulations to investigate the incorporation of cobalt in BiFeO$_3$, as a route to engineer its band gap, band alignment, and ferroelectric polarization. We discuss the thermodynamic aspects of the Co/Fe substitutions, in particular the stability of the solid solution with respect to phase separation. We examine the impact of cobalt substitution on the magnitude of the BiFeO$_3$ spontaneous polarization, which can improve charge separation and can potentially be used to engineer the band alignment for photocatalysis. We calculate the depolarization field in a BiFeO$_3$ thin film with the surface normal parallel to the polarization direction, and discuss the interplay between polarization and band alignment. In the light of our simulation results, we also discuss conflicting experimental results in the literature about the band gap, band alignment, and polarization of these materials.

### 2. Results and Discussion

#### 2.1. Structural and Electronic Properties

Calculated structural and electronic parameters of pure BiFeO$_3$ are shown in Table 1 in comparison to experimental values. As noted before,$^{[4]}$ the screened hybrid functional (HSE) leads to good agreement with experiment in terms of both crystal structure and band gaps. The calculation in the generalized-gradient approximation (GGA) leads to a too narrow bandgap of 1.1 eV. The GGA+$U$ approach (with $U_{\text{eff}} = 4$ eV) leads to more reasonable value (2.3 eV), albeit still below the most accepted experimental range of 2.6–2.8 eV measured at ambient conditions.
conditions. The HSE band gap, 2.9 eV, is slightly above that range. However, it should be noted that there is still a lot of uncertainty about the band gap of BiFeO$_3$, with values as low as \( \approx 2 \text{ eV} \) or as high as \( \approx 3 \text{ eV} \) reported in the experimental literature for this compound, depending on synthesis conditions, particle size and morphology, and measurement method.[27,31] For example, smaller nanoparticles tend to have narrower band gaps.[32] The band gap of BiFeO$_3$ also decreases substantially with temperature, e.g., from about 2.5 eV at ambient temperature to about 1.5 eV at 550 °C.[33] The value of 2.9 eV obtained here for bulk BiFeO$_3$ from HSE calculations seems therefore to be a more reasonable zero-Kelvin prediction than the GGA+U value of 2.3 eV. We have checked that, while increasing the value of \( U_{\text{eff}} \) from 0 to 4 eV leads to a nearly linear increase in bandgap, going beyond \( U_{\text{eff}} = 4 \text{ eV} \) increases the gap more slowly, so unrealistically high values of \( U_{\text{eff}} \) would be needed for the GGA+U calculation to match the HSE result. We therefore keep the widely used value[34-37] of \( U_{\text{eff}} = 4 \text{ eV} \) for correcting the Fe 3d levels when using GGA+U.

The band structure (Figure 2a) and density of states (DOS) (Figure 2b) show that the contribution of O 2p orbitals dominate the valence band (VB) edge and the contribution of Fe 3d orbitals dominate the conduction band (CB) edge. The bottom of the CB is located at the Z point of the Brillouin zone. The VB has two maxima at roughly the same energy, one between F and F, and the other at the Z point (the difference between the two is less than 10 meV). Both spin channels exhibit the same total DOS due to the antiferromagnetic arrangements of the magnetic moments (Fe 3d contributions with opposite spins at the same energy level come from different atoms). There is a large exchange splitting of \( \approx 9 \text{ eV} \) between the occupied and empty 3d orbitals of a given Fe atom, therefore the occupied Fe 3d orbitals are not shown in the DOS plot.

We then considered the substitution of one or two Fe atoms in the 2 \( \times \) 2 \( \times \) 2 supercell by Co, in such a way that the stoichiometry of the solid solution is BiCo$_{0.062}$Fe$_{0.938}$O$_3$ or BiCo$_{0.125}$Fe$_{0.875}$O$_3$. These compositions are within the experimentally observed range (0 \( < x \) \( <0.2 \)) of the rhombohedral phase of the BiCo$_{x}$Fe$_{1-x}$O$_3$ solid solution (upon increasing \( x \), the solid solution has been observed to transition to the tetragonal structure of pure BiCoO$_3$, via an intermediate monoclinic structure[38] although theoretical calculations suggest a more complex behavior at intermediate compositions[39]). The DOS plot for BiCo$_{0.062}$Fe$_{0.938}$O$_3$ (Figure 2c) shows the presence of an empty impurity level of Co 3d character that reduces the band gap from 2.9 to 2.1 eV.

The supercell with composition BiCo$_{0.125}$Fe$_{0.875}$O$_3$ (two Co substitutions in the supercell) has only five symmetry inequivalent configurations. The DOS plots for those configurations (Figure 3) are very similar to the DOS plots for lower Co concentration, but with larger peaks in the Co 3d gap state, whose energy position does not change appreciably with the relative position of the Co atoms in the structure. In these calculations, the magnetic moments of the Co ions were given the same orientation of the magnetic moments of the Fe ions they replace, thus keeping the G-type antiferromagnetic pattern; this accounts for the different relative orientations of the Co magnetic moments over the configurations (i.e., they are parallel in the configurations shown in Figure 3a–c, but antiparallel in d and e). In the next section, we use the relative energies of these configurations to create a model to investigate the equilibrium distribution of Co substitutions.

### 2.2. Thermodynamics of Cation Distribution

For the thermodynamic analysis of the Co distribution, the DFT total energies of the five distinct configurations of double substitutions were mapped into an Ising-like Hamiltonian

\[
E = E_0 + \sum_{i,j} J_{ij} S_i S_j
\]

(1)

where the “spin” variable \( S_i = 1 \) if site \( i \) is occupied by Co, and \( S_i = 0 \) if it is occupied by Fe, and the \( J_{ij} \) values characterize the strength of Co–Co interactions. Note that the spin variables and the Hamiltonian itself are unrelated to the magnetism of the

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**Figure 2.** a) Band structure and b) projected DOS of pure BiFeO$_3$; and c) projected DOS of BiCo$_{0.06}$Fe$_{0.94}$O$_3$ obtained with the HSE functional.
Figure 3. Co positions and projected DOS (from HSE calculations) for the five symmetrically distinct configurations of BiCo0.06Fe0.94O3 studied in this work. Color scheme: Bi = purple, Fe = brown, Co = blue, O = red.

system but simply describe the interactions between Co impurities. Four $J$ constants, corresponding to four different Co–Co distances, plus the $E_0$ values, are then obtained from the five DFT energies, by solving the system of five linear equations with five variables.

The interaction parameters $J$ as a function of Co–Co distance ($d$) are shown in Figure 4a. Clearly, the interaction between impurities is more attractive when the distance between them is shorter. To study the effect of these interactions on the equilibrium cation distribution at specific temperatures, we performed Monte Carlo simulations in a larger ($10 \times 10 \times 10$) supercell with the same composition, BiCo0.06Fe0.94O3. At $T = 500$ K, Co impurities aggregate as one pure-Co spherical cluster per simulation cell (Figure 4b). The formation of such small separate Co clusters is, of course, an artifact from the simulation cell size; using a larger simulation cell would lead to larger and more separated Co clusters. The result from the Monte Carlo simulation simply indicates that there is a thermodynamic preference for Co aggregation, which would lead to complete phase separation at that temperature. Our simulations at $T = 1000$ K (and even at 2000 K) still led to Co impurity aggregation forming single clusters, albeit with a less compact shape and not so well-defined borders. Only at unrealistically high temperatures does the equilibrium cation distribution become more homogeneous.

While these simulations show that there is a strong thermodynamic drive toward phase separation, they implicitly force the BiCoO3 clusters to remain in the rhombohedral structure of BiFeO3. In reality, it would be thermodynamically favorable for BiCoO3 to separate forming its preferred crystal structure, which is tetragonal. To quantify the thermodynamic stability of the BiCoFe1−xO3 solid solution against phase separation to rhombohedral BiFeO3 and tetragonal BiCoO3 phases, we have calculated the enthalpy of mixing per formula unit of BiFe1−xCoxO3 with respect to the pure compounds using the equation

$$\Delta H_{\text{mix}} = E[\text{BiFe}_{1-x}\text{Co}_x\text{O}_3] - (1 - x)E[\text{BiFeO}_3] - xE[\text{BiCoO}_3]$$

(2)

where the $E$ values are the DFT energies per formula unit for the corresponding compositions, at their ground-state structures. For $x = 0.0625$, we obtain $\Delta H_{\text{mix}} = 0.027$ eV per formula unit. As is common in the description of very dilute solid solutions, we can write that for small values of $x$

$$\Delta H_{\text{mix}}(x) = Wx$$

(3)

where $W = 0.43$ eV is the solution energy. From this value, we can estimate the thermodynamic solubility limit $x_s$ of Co in BiFeO3, as the minimum of the free energy of mixing (including $\Delta H_{\text{mix}}(x)$ and the configurational entropy contribution) at a given temperature, which is

$$x_s \approx e^{-\frac{W}{k_B T}}$$

(4)

For example, at $T = 600$ K, $x_s = 0.00026 = 260$ ppm. Therefore, Co substitution in BiFeO3 can be expected to be thermodynamically stable against phase separation only at trace amounts.

However, it is important to realize that even when phase separation is thermodynamically preferred, homogenous solid solutions can still exist, protected by the very slow kinetics of cation diffusion. Cation exchange barriers are well known to be very high, typically $\approx 2$ eV or above for ionic solid solutions. For example, values of 193, 200, and 230 kJ mol$^{-1}$ have been estimated from experimental measurements of cation exchange kinetics in (Fe$_{0.5}$Mn$_{0.5}$)$_2$SiO$_4$ olivines,[42] (Fe$_3$O$_4$)$_x$(MgAl$_2$O$_4$)$_{1-x}$ magnetite-spinel solid solutions,[43] and disordered MgAl$_2$O$_4$. 

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spinels,[44] respectively. These high activation barriers mean that cation exchange typically only starts, at any measurable rate, if samples are heated above \( \approx 700 \) K, whereas full equilibrium (involving either ex-solution or ordering) is only reached at much higher temperatures. For Co-substituted BiFeO\(_3\), we have not calculated cation exchange activation barriers (such calculations are not trivial, because the mechanism for cation exchange may involve the collective movements of many atoms and/or be mediated by vacancies or other defects), but it can be safely expected that they would be similarly high. Therefore, while there is clearly a thermodynamic driving force for ex-solution in Co-substituted BiFeO\(_3\), such separation process would only be observable if samples are treated at high temperatures. When a homogenous solid solution is prepared, it should remain stable (or more precisely, metastable) if kept at ambient or only moderately high temperatures. An example of such metastable oxide solid solution used as a functional material is Ce\(_{1-x}\)Zr\(_x\)O\(_2\),[45] which is thermodynamically unstable with respect to phase separation into Ce-rich and Zr-rich oxides at most compositions, but still can be synthesized as a homogenous solid solution that is widely used in catalysis at moderate temperatures.[46,47]

### 2.3. Ferroelectric Properties

To study the effect of cobalt substitution on ferroelectric properties of BiFeO\(_3\), we calculate the spontaneous polarization \( P \) from first principles. The Born effective charge (BEC) tensor for atom \( j \), \( (Z_{\alpha\beta}^j) \) is defined as the derivative of the polarization \( P \) with respect to the atom coordinates (at zero electric field \( \epsilon \))

\[
Z_{\alpha\beta}^j = \left. \frac{\partial P_\alpha}{\partial u_{j\beta}} \right|_{\epsilon=0}
\]  

(5)

where \( \alpha \) and \( \beta \) are Cartesian indices, and can be obtained using density functional perturbation theory.[48] Then, to estimate spontaneous polarization we compute the Cartesian components of the polarization \( P_\alpha \) as

\[
P_\alpha = \frac{Z}{V} \sum_{\alpha\beta} Z_{\alpha\beta}^j \Delta u_{j\beta}
\]  

(6)

where

\[
Z_{\alpha\beta}^j = \frac{1}{\xi} \int_0^\xi Z_{\alpha\beta}^j (\xi') d\xi'
\]  

(7)

is the average of the BEC tensor over the values of the distortion parameter \( \xi \) that connects the ferroelectric \( R3c \) phase (\( \xi = 1 \)) and the reference, centrosymmetric \( R-3c \) phase (\( \xi = 0 \)); \( \Delta u_{j\beta} \) is the displacement of ion \( j \) in the Cartesian direction \( \beta \). This approach to calculate the polarization avoids the more expensive Berry-phase calculations based on the modern theory of polarization,[49,50] but previous work on similar systems has shown that both approaches give very similar results.[51] The polarization calculated at different distortion points is shown in Figure 5.

For pure BiFeO\(_3\), we obtained 109 \( \mu \)C cm\(^{-2}\), and it increases to 143 \( \mu \)C cm\(^{-2}\) for BiCo\(_{0.06}\)Fe\(_{0.94}\)O\(_3\) (there is only one Co atom per supercell at this composition, and there is only one symmetrically distinct Fe site, so the result does not depend on the substitution site). Let us first discuss the value for the pure compound. It is well known that experimental measurements of polarization in this material have led to a very wide spread of results (e.g., Table I in ref. [7] lists experimental values from different sources ranging from 2.2 to 158 \( \mu \)C cm\(^{-2}\)). There are several causes for
BiFeO$_3$ polarization, we turn to the experimental results presented closest to these best estimations. In ref. \cite{13}, a GGA reticale estimation of the effect of Co on the electric polarization are important in the behavior of the polarization in this system. Served strong deviations indicating that nonionic effects

$$B = \sum_{i} q_i e_i$$

where $q_i$ is the formal charge and $e_i$ is the electron charge. Bader charges would approach the formal charges, so the observed variations in $\mu_C$ are due to the electronic structure of the element and the surrounding atoms. The Bader charge of Co ($+1.51$) is significantly different from the formal charge ($+2$) of Co in the compound. The Bader charge of Fe ($+1.71$) is closer to the formal charge ($+2$) of Fe in the compound. In a more ionic system, both the Born effective charges and the Bader charges would approach the formal charges, so the observed deviations indicate that nonionic effects are important in the behavior of the polarization in this system.

Interestingly, there are disagreements between previous theoretical estimations of the effect of Co on the electric polarization in BiFeO$_3$. In ref. \cite{13}, a GGA+U calculation with a higher value of the Hubbard parameter for Co 3d orbitals, $U_{eff} = 6$ eV, compared to the value used in this work, $U_{eff} = 3.3$ eV, did not lead to much difference in polarization between pure and Co-substituted BiFeO$_3$. We have not been able to reproduce their results exactly (there are other differences in methodology), but when we

Use their $U_{eff}$ value we observe a much smaller enhancement (±50% of ours) of the polarization upon Co substitution. On the other hand, an earlier study by Sui et al., \cite{54} also based on GGA+U calculations but with a different functional (PBEsol)\cite{55} and a different $U_{eff}$ value (8 eV), did conclude that Co substitution would lead to an enhancement of the polarization of BiFeO$_3$. The effect of the functional, the $U_{eff}$ value, and other calculation settings on the estimated polarization deserves further study.

2.4. Band Alignment and Applications in Photocatalysis

To explore the activity of these compounds in photocatalytic applications, it is important to estimate the positions of the VB maximum and the CB minimum in an absolute scale, e.g., relative to the vacuum level. This is necessary to obtain the relative energies of these band edges with respect to half-reaction potentials for the redox reactions of interest, e.g., water splitting. However, energy levels obtained from the bulk calculation are given relative to the average electron potential in the solid. To align the electronic structure with reference to the vacuum level, we determine the potential difference $\Delta V$ between the vacuum potential and the pseudo-bulk average using an auxiliary slab calculation. In the first instance, to ignore the effect of ferroelectric polarization, we have used a symmetric and stoichiometric slab terminated by the nonpolar (110) surface, for which the vacuum level is the same at both sides of the slab (Figure 6).

The calculated positions of the band edges of BiFeO$_3$ and BiCo$_{0.06}$Fe$_{0.94}$O$_3$, with respect to vacuum potential are shown in Figure 7. We can compare these with the half-reaction potentials for water splitting, corresponding to the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER)

$$2H_2O \leftrightarrow H_2(g) + \frac{1}{2}O_2(g) + 2e^-(OER) \tag{9}$$
In the vacuum scale and at pH = 0, the HER level is located at \(-4.44\) eV, and the OER level is located at \(-5.67\) eV. At temperature \(T\) and \(pH > 0\), these energy levels are shifted up by \(k_BT \times pH \times \ln10\). For \(pH = 7\) and room temperature, the HER level is then located at \(-4.03\) eV and OER level is located at \(-5.25\) eV, respectively. For a water-splitting photocatalyst made of a single semiconductor, the positions of the CB minimum and the VB maximum should straddle those half-reaction potentials. The band edges of BiFeO\(_3\) and BiCo\(_{0.06}\)Fe\(_{0.94}\)O\(_3\) and the water redox potentials are shown in Figure 7. The calculated band edges are not well aligned with the half-reaction potentials for water splitting, because the CB edges are too negative with respect to the HER level, suggesting that these materials are not suitable as single-semiconductor photocatalysts for the full water-splitting reaction. However, according to this result, BiFeO\(_3\) can be used as a photoanode in a PEC cell, for the water oxidation reaction.

When comparing our band alignment with experiment, we must recall that to build band alignment diagrams, experimentalists measure or estimate at least two out of four properties: the ionization potential (IP), the electron affinity (EA), the band gap (\(E_g\)), and/or the electronegativity (which is defined here as \(\chi = \frac{1}{2}(IP + EA)\)). The relation between these quantities and the band edges \(E_{\text{CB}}\) and \(E_{\text{VB}}\) is given by the equations

\[
E_{\text{CB}} = -EA = -\chi + \frac{1}{2} E_g
\]

(10)

\[
E_{\text{VB}} = -IP = -\chi - \frac{1}{2} E_g
\]

(11)

Usually, the optical band gap is measured, and one of the other three properties is also obtained, to complete the band diagram. Given that there are wide differences in measured band gaps, and that there are various ways to measure or estimate the other properties, strong discrepancies in the band alignments reported for BiFeO\(_3\) in the experimental literature are not surprising. For example, Ji et al.\(^{[18]}\) calculated the IP of BiFeO\(_3\) from the ultraviolet photoelectron spectrum (by subtracting the width of the spectrum from the exciting photon energy). Combined with a band gap of 2.74 eV, that measurement led to a CB edge at \(-3.56\) eV and a VB edge at \(-6.30\) eV in the vacuum scale, which do straddle the water-splitting redox potentials. A similar band alignment for BiFeO\(_3\) band edges with vacuum had been proposed before by Wu and Wang.\(^{[56]}\) These authors measured an optical band gap of 2.73 eV, and estimated the EA at 3.33 eV following Clark and Robertson,\(^{[57]}\) who had proposed that value from a simple comparison with SrBi\(_2\)Ta\(_2\)O\(_9\). That leads to a CB edge at \(-3.33\) eV and a VB edge at \(-6.06\) eV in the vacuum scale, also straddling the water-splitting redox potentials. However, the EA of BiFeO\(_3\) seems to be significantly underestimated in those studies. Measurements by Moniz et al.\(^{[29]}\) using electrical impedance spectroscopy and a Mott–Schottky plot\(^{[58]}\) led to an EA of 4.62 eV. That value means that the band edges of BiFeO\(_3\) do not straddle the water-splitting redox potentials, the CB edge being too negative. This result also agrees with the simpler estimation of band positions made by Li et al.\(^{[59]}\) using the electronegativity \(\chi\) of the oxide calculated as the geometric mean of the electronegativities of the constituent atoms, and a measured band gap of 2.19 eV, from where they arrive at an EA of 4.94 eV. The same method has been applied by other authors, using slightly different band gaps.\(^{[17,25]}\) Kolivand and Sharifinia\(^{[25]}\) confirmed the value determined by this method (EA = 4.84 eV) with their own Mott–Schottky plot analysis. Interestingly, if we use our HSE band gap, the average electronegativity method leads to almost the same band positions that we obtain from the HSE calculation in the auxiliary slab.

Table 3 summarizes EA estimations from the literature in comparison with our theoretical results. Our results agree with the higher EA estimations in the literature from Mott–Schottky measurements (albeit with some overestimation). The comparison with experiment is complicated by the fact that the theoretical results correspond to zero-Kelvin calculations in the bulk solid, whereas experiment results refer to finite temperature measurements, typically in nanostructured materials. Furthermore, different surface facets of a material have different values of IP/EA due to different surface dipoles.\(^{[59]}\) Often the measurements reported are on polycrystalline materials with many surface facets and therefore measured band edges will either be ensemble averages or possibly even the shallowest levels in the system.

Besides the above-mentioned caveats, our findings give support to the conclusion that unmodified BiFeO\(_3\) cannot be used as a single-semiconductor photocatalyst for water splitting, because the EA is too high (the CB is too negative) to drive the hydrogen evolution half-reaction. Cobalt substitution does not help on this issue, because the low-lying empty Co 3d levels increase the EA and lower the CB further, as seen in Figure 7. However, as mentioned earlier, BiFeO\(_3\)-based systems can be useful as photoanodes in PEC cells, because of the highly oxidizing VB holes; effective coupling with a photocathode for the HER could make an efficient tandem system. BiFeO\(_3\) can also be used for water splitting in heterojunctions with other semiconductors like CdS, as demonstrated by Kolivand and Sharifinia.\(^{[25]}\) They showed that pure BiFeO\(_3\) was not photocatalytically active for the full water-splitting reaction, which is consistent with our theoretical band alignment. When BiFeO\(_3\) is in a heterojunction with CdS, which has a lower EA (they estimate \(\approx 4\) eV), a direct Z-scheme\(^{[40]}\) band alignment is obtained, which allows unassisted water splitting without using any sacrificial agents. In principle, for such heterojunctions, Co substitution in BiFeO\(_3\) might be advantageous, because the band gap narrowing with respect to the pure compound would allow more efficient visible light absorption at the BiCo\(_{0.8}\)Fe\(_{0.2}\)O\(_3\) end of the heterojunction, while
Table 3. Estimations of the electron affinity (EA) of BiFeO$_3$ reported in the literature, in comparison with the values obtained in this work. In some of the original papers, values are reported with respect to the normal hydrogen electrode (NHE), and have been converted here to the vacuum scale for easy comparison.

| Source                        | EA [eV] | Method                                                                 |
|-------------------------------|---------|------------------------------------------------------------------------|
| Clark & Robertson (2007)      | 3.33    | Comparison with SrBi$_2$Ta$_2$O$_9$                                    |
| Wu & Wang (2010)              |         |                                                                        |
| Li et al. (2009)              | 4.94    | Band gap measured and electronegativity estimated from elements        |
| Ji et al. (2013)              | 3.56    | Band gap measured and ionization potential from ultraviolet photoelectron spectrum |
| He et al. (2013)              | 5.01    | Band gap measured and electronegativity estimated from elements        |
| Moniz et al. (2014)           | 4.62    | Electrical impedance spectroscopy and Mott–Schottky plot               |
| Kolivand & Sharifnia (2020)   | 4.84    | Band gap measured and electronegativity estimated from elements; Mott–Schottky plot |
| This work                     | 5.13    | DFT (HSE) calculations in bulk and auxiliary slab                      |

Figure 8. BiFeO$_3$ slabs with (111) surface terminations and the planar average electrostatic potential for a) centrosymmetric (R-3c) phase and b) polar (R3c) phase.

the more negative CB in the solid solution, compared to the pure oxide, would reduce the losses associated with the interfacial electron–hole recombination. However, our results suggest that the CB in the Co-substituted system might be too low to drive the water oxidation reaction, although our calculation seems to somewhat overestimate the EA values, so it is difficult to establish a firm conclusion. Furthermore, it is unclear to what extent Co impurities could act as a trap state for photogenerated electrons, which would be detrimental for photocatalytic activity.

Our analysis above has focused on water splitting, but BiFeO$_3$-based systems could also be used as photocatalysts for other reactions, potentially even without help from heterojunctions. For example, the production of hydroxyl radicals from water for oxidation of organic pollutants might be a more suitable reaction.\[61\] These HO radicals can be useful for the degradation of effluents from textile and pharmaceutical industries. The relevant redox pairs and the energy levels of the half-reactions are also shown in Figure 7. Our calculated band edges for BiFeO$_3$ do not quite straddle the half-reaction potentials, but because our EA value is likely to be slightly overestimated, the position of the band edges might be right for this reaction. It is therefore not surprising that, as discussed in the Introduction, there is already a large body of experimental work trying BiFeO$_3$-based photocatalysts for the degradation of organic pollutants.\[19\]

Finally, we discuss the effect of the ferroelectric polarization on the photocatalytic properties, in a very simplified picture. The above band alignment calculation, based on a symmetric nonpolar slab along the [110] direction, ignores any interplay between the band alignment and ferroelectric polarization effects. We therefore construct another slab, now along the polarization ([111]) direction. The surface termination of the slab is such that the only dipolar moment comes from the ferroelectric distortion: the slab with equivalent surface termination for the centrosymmetric phase (R-3c) is nonpolar (Figure 8a). In the slab for the ferroelectric R3c phase (Figure 8b), the macroscopic average potential exhibits a gradient $dV/dz = 0.064$ V Å$^{-1}$, which represents the depolarization field that arises to compensate for the surface dipole. (A correction to the potential was required here to accommodate the slab dipole within the periodic boundary conditions of the calculation).\[62\] This depolarization field creates a drive to
separate photogenerated charge carriers, which can be expected to be beneficial for photocatalytic (and photoelectronic) applications.

The presence of the depolarization field also has implications for the electronic band alignment, because it leads to a shift in the band positions on the surfaces of an isolated thin film, which is proportional to the magnitude of the field and to the thickness of the film. For example, given the calculated field intensity of $\approx 64$ mV Å$^{-1}$, a BiFeO$_3$ film that is, e.g., $\approx 2$ nm thick in the polarization direction, would exhibit a band shift of $\approx 1.3$ eV between its two surfaces. Such a shift is larger than the misalignment of the CB of BiFeO$_3$ for the HER. In the Co-substituted film, where the polarization is stronger, the depolarization field intensity will also be higher, but the shift needed to bring the CB of Co-substituted BiFeO$_3$ above the HER level is also $\approx 0.8$ eV larger than for pure BiFeO$_3$. Assuming a depolarization field proportional to the magnitude of the polarization, we estimate that bringing the CB of Co-substituted BiFeO$_3$ to the same level above the HER would require a thicker film, of $\approx 4$ nm.

The above discussion illustrates how polarization may affect the photocatalytic properties of BiFeO$_3$, not only in terms of aiding charge separation but also in terms of controlling band alignment: the direction of polarization can be used to control the position of the electronic levels at a given BiFeO$_3$ surface or interface. There are, of course, many other factors that we have not considered here. For example, in practice these films may attract free carriers from the surroundings that would partially or totally compensate the electric field. In the Co-substituted films, there may be inhomogeneities of the Co distribution, potentially including phase-separated regions with higher Co concentration. The present model constitutes only an initial approximation to the theoretical modeling of what is undoubtedly a very complex phenomenon.

3. Conclusions

We have discussed here the response of the multiferroic material BiFeO$_3$ to Co substitution in Fe positions, considering electronic, magnetic, and thermodynamic aspects, as well as potential applications in photocatalysis. Co/Fe substitutions are an interesting strategy to modify the functional behavior of BiFeO$_3$. The band gap of the system is significantly reduced as a result of Co substitution, from 2.9 eV to around 2.1 eV, and there is a simultaneous enhancing of the spontaneous polarization. This large enhancement of ferroelectricity in this system would further promote effective carrier separation in applications such as photovoltaics or photocatalysis. Our Monte Carlo simulations show that Co$^{3+}$ ions would tend to aggregate at the concentrations studied here if an equilibrium distribution can be reached, although this phase separation is likely to be kinetically limited by cation diffusion barriers at most temperatures of interest for applications. Our calculations support the conclusion that the high electron affinity of BiFeO$_3$ makes the conduction band too negative in comparison with the level for the HER. Therefore, unmodified BiFeO$_3$ cannot photocatalyze the full water-splitting reaction. However, it can be used as a photoanode for water oxidation in photoelectrochemical cells, in combination with a suitable photocathode for the HER. Direct Z-schemes with semiconductors with lower electron affinity could also be used for the full water-splitting reaction, and we argue that Co/Fe substitutions might improve the performance of BiFeO$_3$ in such composite photocatalysts, although with some caveats in terms of band alignment and trap state effects which require further investigation. We quantify the large electric fields formed in these materials, associated with the ferroelectric distortion, and demonstrate how these fields can affect the electronic level positions. BiCo$_{0.2}$Fe$_{0.8}$O$_3$ solid solutions deserve further theoretical and experimental investigation in terms of its photocatalytic applications.

4. Experimental Section

**DFT Simulations**: DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP) [63,64]. For geometry relaxations, substitution thermodynamics, and for the electronic structure calculations, a screened hybrid functional, based on the functional by Heyd, Scuseria, and Ernzerhof (HSE06) was used [65] which admixed the exact nonlocal exchange from the Hartree–Fock theory, screened at long-range with a screening parameter of 0.2 Å$^{-1}$, into the local Perdew–Burke–Ernzerhof (PBE) functional [66] of the GGA. In this case, 20% Hartree–Fock–exchange (instead of the 25% proposed in the original HSE06 functional) was chosen, following Shimada et al. [67] who showed that these settings led to good agreement with experiment in terms of both structural parameters and band gap. The screened hybrid functional used here simply as HSE was referred.

For the calculation of Born effective charges and polarizations, which is computationally demanding, the less expensive GCA+U approach was used, where Hubbard effective parameters ($U_{\text{eff}}$) of 4 and 3.3 eV were applied to the 3d orbitals of Fe and Co, respectively; these values were originally fitted to reproduce the oxidation energies of the corresponding binary transition metal oxides [68] and have been found to transfer well to describe the properties of more complex oxides of these metallic elements [35–37].

The projected augmented wave (PAW) method [69,70] was used in all calculations to describe the interactions between the valence electrons and frozen cores, by explicitly treating 15 valence electrons for Bi, 8 for Fe, 9 for Co, and 6 for oxygen. An energy cutoff of 520 eV was used to truncate the plane wave expansion of the Kohn–Sham wavefunctions, which was 30% above the default cutoff for the employed PAW potentials, to minimize Pulay errors. Brillouin zone (BZ) integrations were performed by sampling the reciprocal space using a Γ-centered mesh of 4×4×4 k-points with reference to the rhombohedral unit cell, and commensurate grids for supercells. The only exception was the structural relaxations, using the HSE functional, of the different Co-substitution configurations in the 2×2×2 supercell, which were performed using Γ-only calculations. In all cases, the cell parameters were allowed to relax, and the ions were moved toward equilibrium until the Hellmann–Feynman forces were less than 0.01 eV Å$^{-1}$.

The DFT calculations were all spin-polarized, and the G-type antiferromagnetic ordering was assumed, as well as collinear spin arrangements, i.e., the small effect of spin canting in BiFeO$_3$ was ignored. Both Fe(III) and Co(III) cations were initialized in high-spin (HS) configurations, which the calculations conserved after convergence. Iron in BiFeO$_3$ is well known to be in HS Fe(III) configuration, unless high pressures are applied, in which case a transition to low-spin (LS) takes place [71,72]. The spin state of Co(III) (a d$^7$ cation) in BiCo$_{0.2}$Fe$_{0.8}$O$_3$ has been more disputed in the literature. In the pure-Co end-member, BiCo$_2$O$_4$, Co(III) is in HS state at ambient pressure and low temperatures [73]. But Ray et al. concluded, from magnetization measurements, that dilute Co in BiFeO$_3$ at low temperature (below 150 K) and low external magnetic field, was LS [74]. On the other hand, from a combination of magnetic measurements and DFT calculations, Fan et al. concluded that at ambient temperature the LS state of Co(III) in this system was unfavored, and their GGA+U calculations indicated that HS Co(III) was more stable than LS Co(III) in BiFeO$_3$. [75] Their test calculations using the HSE functional in the supercell with one Co substa-
tution showed that HS Co(III) was more stable than LS Co(III) in BiFeO₃, by \( \approx 0.2 \) eV. Therefore, HS Co(III) was used in all the calculations.

**Thermodynamics of Cation Distribution:** The symmetrically distinct Co substitution configurations were found using the SOD (Site Occupancy Disorder) program.²⁹,³⁰ Two configurations were considered equivalent if they were related by a symmetry operator, and the group of symmetry operators of the supercell consisted of the original symmetries of the unit cell and their combinations with supercell translations. The magnetic moment of the Co cation was assumed to have the same orientation as that of the replaced Fe cation. In this case, the inequivalence between spin-up and spin-down Fe atoms did not increase the number of symmetrically different configurations: all possible pair distances were considered, and the G-type antiferromagnetic ordering implies that there is only one type of relative magnetic orientation for a pair at a given distance (e.g., each pair in the pseudo-cube edge has antiparallel spins, each pair along the diagonal of the pseudo-cube face has parallel spins, etc.).

The DFT energies of the symmetrically independent configurations were used to fit an effective Hamiltonian model, which was then used to perform Monte Carlo simulations in a large \( (10 \times 10 \times 10) \) supercell with the same composition, BiCo₁₀⁺Fe₀₉⁻O₃, using the GULP code.²⁵,²⁶ At each step of Monte Carlo simulation, a configuration was created by randomly swapping a pair of atoms, which corresponded to an energy difference \( \Delta E \). The new configuration was accepted, following the Metropolis algorithm,²⁷ with probability \( p = \min \{1, \exp(-\Delta E/k_B T)\} \), where \( k_B \) is Boltzmann’s constant and \( T \) is the temperature. 40 million steps were used to achieve equilibrium, and the simulations were performed at \( T = 300 \), 1000, and 2000 K.

**Band Alignment:** For the alignment of the band edges of BiFeO₃ with respect to vacuum, periodic slab models with different terminations, separated by a vacuum gap of 15 Å in the periodic supercell were built. The MacroDensity code⁷¹ was used for calculating the planar averages of the electrostatic potential in planes parallel to the slab surface, to determine the potential difference between the bulk (average in the middle of the slab) and the vacuum level (in the middle of the vacuum gap). For the alignment of the band edges of BiCo₁₀⁻FeₓO₃, slabs with Co/Fe substitutions were not created, but the core levels of bulk Fe atoms were simply aligned far from Co substitutions.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

The work was designed by R.G.C., K.T.B., and U.V.W. The DFT calculations were done by S.G. All authors contributed to the interpretation and discussion of the results. The first draft was written by S.G. and R.G.C. All authors contributed to the final manuscript.

**Data Availability Statement**

The data that support the findings of this study are openly available in Zenodo at https://doi.org/10.5281/zenodo.5720628, reference number 5720628.

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