Free Energy Landscape Approach to Aid Pure Phase Synthesis of Transition Metal (X = Cr, Mn and Fe) Doped Bismuth Titanate ($\text{Bi}_2\text{Ti}_2\text{O}_7$)

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ABSTRACT

A density functional theory study of Cr, Mn and Fe substitutions in $\text{Bi}_2\text{Ti}_2\text{O}_7$ (BTO) photocatalysts is presented. We performed a stability analysis from our total energy calculations and have determined formations of dopant inspired phases are detrimental to the overall photocatalytic performance of X-doped BTO. From our calculated formation energies and electronic structures it is shown that X substitution of Ti is least stable and should be associated with formation of secondary phases more so than X substitution of Bi. This result contradicts the many experimental studies which suggest transition metal dopants always substitute Ti in BTO, but on the other hand, explains the poor photocatalytic response beyond what has become known as the *critical* dopant concentration.

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1. Introduction

Photovoltaic (PV) current production and photo-electrochemical (PEC) fuel production need materials with high rates of photoexcited charge transfer resulting from absorption of photons in the visible range. The challenge in developing such materials is to reduce their band gaps while maintaining minimal distortion of their underlying lattice symmetries. Ternary and higher order metal oxides have garnered much attention lately because they are so readily stabilized into different morphologies that possess an array of functional properties. However this propensity for phase transition is detrimental to the enhancement of these materials' functionality. For example, efforts to enhance the photocatalytic property of tungstates [1–4], tantalates [5–8], vanadates [9–13], and titanates [14–20] are shown to be limited by the vulnerability of transition prone crystalline phases. Evidently, the slightest phase gradient such as a single intrinsic defect can have significant effects on the functionality of a material because it only takes one to be a charge trap that significantly increases the recombination rates.

X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) are the standard techniques of comprehensive material characterization. XRD is used to determine if a material possesses enough crystalline features to be categorized within a specific space group and XPS is used to determine if the components of that material possess the interactions to be categorized within a specific stoichiometry or charge state. However, the detection limits of these methods render them useless for detecting just the onset of a secondary phase, especially in complex materials [21,22]. For instance, main peak angular position shifts as small as 0.1° are detectable with the fastest scan rates for binary metal oxides and would be attributed to the early formation of a secondary phase. For ternary and higher order oxides, shifts of this magnitude are only observed when the scan rate is very slow and are almost always attributed to strain effects or

improper setup. Shifts in FWHM are also pseudo-ambiguous in this way when used to determine the onset of an unwanted phase. The magnitude of shift typically observed in multi-metal oxides is commonly attributed to changes in grain size, instead of fewer reflections of a desired plane as they are for binary oxides. Thus any increase in quantum yield is then due to size effects instead of modification of the electronic structure. For this reason, we seldom see doping of multi-metal oxides exceed concentrations greater than 1-2 wt. % before a full blown secondary phase is formed.

Coincidentally, the *critical* dopant concentration ranges between 1-2 wt. % for doping of mixed metal oxides, especially for those synthesized using hydrothermal techniques [3,4,6,17,23–29]. Hydrothermal synthesis is the *go-to* method for producing single phase multi-metal oxides which depends on high pressure solubility of precursor materials in hot water. Therefore modeling based on density functional theory (DFT) is often overlooked on account of its inability to address the associated kinetic effects. However, pressure effects, which persist in equilibrium conditions, and affect the chemical environment, can be modeled with DFT. One method in particular includes interpolating the effects of varying atomic free energies. For instance, in a growth process where O partial pressure is extremely reduced, stable configurations with X^{3+} cations may in some adiabatic process require reduction of the X cation to a 2+ charge state, or formations of O vacancies to compensate any charge imbalances. Such effects of low O partial pressure are modeled here by calculating the formation energy of X-doped $\text{Bi}_2\text{Ti}_2\text{O}_7$ (BTO) using a lower limit of available O free energy. Conversely, increased O partial pressure may require oxidation of the cation to a 4+ charge state, or formations of O interstitials to accommodate the new charge distribution. This case is modeled here by calculating the formation energy of X-doped BTO using an upper limit of available O free

energy. Given the expression representing formation energy is linear, all intermediate points should then be on the line connecting the two limiting cases. The association of intrinsic defects with the availability of anion free energy follows from well-established theory [30–33] and is most recently demonstrated in other models [34–36].

Bismuth titanate ($\text{Bi}_2^{3+}\text{Ti}_2^{4+}\text{O}_7^{2-}$) with pyrochlore structure has been studied as a photocatalyst that can be used to convert solar energy into H_2 and O_2 (fuels) from water [37–48]. Popularity of BTO's water splitting ability is due to the fact Bi_2O_3 and TiO_2 are its binary analogues (i.e. $\text{Bi}_2\text{O}_3 + 2\text{TiO}_2 = \text{Bi}_2\text{Ti}_2\text{O}_7$). Since the band gap of TiO_2 straddles the redox potentials of water and Bi_2O_3 has a band gap of 2.61eV [49], it is reasonable to expect combining them to form BTO should result in a better photocatalyst. For example, the band gap of BTO should straddle the H_2 and O_2 evolution potentials of water like TiO_2 , but be smaller in size or have high sloping conduction bands like Bi_2O_3 . Indeed the band gap of BTO straddles the redox potentials of water, but the band gap is still wide at 2.8eV [41], and due to the presence of active Bi 6s lone pairs, the unoccupied Bi 6p states are strongly coupled with Ti 3d antibonding states. Ultimately, the band gap and band dispersion of BTO prevent it from being more active in visible light, but there is potential to increase its efficiency as a water-splitter provided the doping limitations and the deficiencies associated with characterization can be overcome.

Recently, Fe doped BTO (Fe-BTO) was hydrothermally synthesized using a surfactant assisted wet chemical reverse micelle-based approach [41]. The synthesized Fe-BTO samples had a linear reduction of the band gap with respect to the wt. % loading of Fe, but H_2 production peaked at around 1 wt. %. XRD analysis indicated formation of Fe_2O_3 at 2 wt. % which suggested formation of the secondary phase had begun before XRD could detect it. In principle, thermodynamic changes within the high pressure autoclave could have promoted doping

configurations that were undetectable using XRD but disruptive enough to be detrimental to the overall photocatalytic output. For instance, BiCl_3 was allowed to flow in to the autoclave as an effort to address the ‘sweating out’ of Bi atoms. This would force a rich supply of Bi, in effect, reducing the likelihood of Bi being substituted by Fe. Also, BiCl_3 is a halide known to possess catalytic properties [50–53] that could easily cause local redox of the cations. Without a theoretical model to explore these possibilities it is impossible to determine the parameter set that would exclude adverse doping configurations.

Likewise, in a synthesis and characterization study of Mn-BTO [44], the authors reported around 1 wt. % Mn loading, the samples showed a band gap reduction of about 0.4 eV. However the H_2 evolution rate, albeit twice that of the Fe-BTO samples, peaked and declined rapidly thereafter. Since the Mn-BTO particles were about 20nm smaller than the Fe-BTO particles, the increase in photocatalytic performance could be attributed to size effects, as the authors suggested. Within a size regime where the exciton radius is greater than one of the particle’s dimensions, shorter charge diffusion lengths and larger reaction sites are expected. However, in terms of phase stability, larger crystals are preferable. Therefore any statement in regards to which dopant, Mn or Fe, is better as a photocatalytic enhancer could not be made. Furthermore, XRD could not detect any abnormality in the architecture of the samples, so it was impossible to definitively characterize the true nature of Mn loading such as which cation it substituted, its charge state, etc.

An experimental study on Cr-doped bismuth titanate has also been done but with different stoichiometric BTO [54]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was synthesized as nano-sheets from another facile hydrothermal approach which the authors claim had a high percentage of reactivity on {110} facets. They attribute the enhanced activity to the increase of photoexcited charge transfer from

Cr 2p impurity levels in the VBM, and claim to have loaded BTO with Cr up to a concentration of 2.1 wt. % ($\text{Bi}_4\text{Ti}_{3-x}\text{Cr}_x\text{O}_{12}$ with $x = 0.4$) before the enhanced photocatalytic performance was halted by a phase gradient. XRD and FT-IR could not detect any effect Cr loading had on the crystallographic phase in this case either. From our theoretical perspective, reduction of BTO's band gap via transition metal loading requires an electronic structure derived understanding of the loading stabilities. If *a priori* knowledge of the effective conditions that control which cation is substituted existed, it would be very beneficial to the quality of complex materials synthesized. Fortunately, thermodynamic modeling provides this valuable information regarding free energy dependence of pure phase stability. Hence, state-of-the-art first principle methods like, DFT, are extremely useful for predicting the chemical parameters which govern pure phase synthesis of multi-metal oxides, or any other multicomponent materials.

In this paper we embrace the opportunity to increase our electronic understanding of doping stability in a complex multi-metal oxide. The free energies derived from our DFT calculations were analyzed to determine the chemical potential ranges that promote single phase stability of Cr, Mn and Fe doped BTO. A systematic study of the different doping configurations along with their electronic structures are provided to help answer the questions experimental characterization alone could not. Questions like: Which cation site is most likely to be substituted by the dopants? How likely are vacancies or interstitials stabilized in conjunction with substitutional doping? What are the signature onsite interactions of A and B-site doping? Which doping configurations can be associated with early phase transition? What thermodynamic limits can be imposed to obtain desired configurations? What X atom is better suited to enhance our material? And, how do we go beyond the critical concentration and maintain a pure phase?

2. Computational Details

Our DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [55–57]. VASP uses the projector augmented wave (PAW) method with the crystal wave functions expanded in terms of a plane wave basis set ($E_{\text{cut}} = 400\text{eV}$) to describe interactions between core and valence electrons. The PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional was used as it is still the best known functional for general accuracy and applicability at the DFT level [58]. In a review of theoretical models that employed custom basis sets [59], the addition of extra exchange energy resulted in a more quantitative description of the electronic properties as they pertained to metal oxide surfaces, however in our case, a qualitative description is sufficient to elucidate the probabilistic nature of transition metal doping in the bulk. The starting atomic coordinates were defined by the BTO unit cell, which consists of 8 $\text{Bi}_2\text{Ti}_2\text{O}_7$ formula units for a total of 88 atoms. Full relaxation (ion position and lattice parameters) of the crystal structures was based on the residual forces between atoms becoming lower than $0.01 \text{ eV}/\text{\AA}$. The Brillouin zone was sampled using a saturated grid density of $5 \times 5 \times 5$. For a cubic structure with a lattice parameter greater than $10\text{\AA}$ in magnitude, this k point sampling was found to be sufficient.

The formation enthalpies (Equation 1) of each structure were defined as the energy difference between its total energy (E_t) and the combination of atomic energies (chemical potentials, μ_i) required to compose the structure; here n_i is total number of i^{th} atoms.

$$\Delta H_f = E_t - \sum_i n_i \mu_i \quad (1)$$

The formation energies for doping were defined as the sum of two differences (Equation 2). The first difference is the total energy difference between the doped unit cell and the pristine unit cell, e.g. the energy gained or loss by forming the defect. The second difference is written in

summation form where each term has an operator α associated with it. This operator becomes either a negative sign or a positive sign depending on the i^{th} atom added or removed to form the cell. By convention if this quantity is an overall negative value then the defect is considered stable and forms spontaneously otherwise the alternative is indicated.

$$E_f(\mu) = E_d - E_t + \sum_i \alpha_i n_i \mu_i \quad (2)$$

For a deeper analytical purpose we considered the variation in an atomic chemical potential due to the atomic sources. Hence μ_i represents the atomic energy plus some additional free energy due to where the atom came from (see Equation 3). When used with Equation 1, a constrained linear equation can be generated that allows us to evaluate formation of X-BTO given different combinations of additional free energy.

$$\mu_i = \mu_i^0 + \Delta\mu_i \quad (3)$$

This scope dictates thermodynamic limits be imposed on the additional free energies. For instance, to avoid solutions to the constrained equation that would result in atomic dissociation, an upper bound on $\Delta\mu_i$ is used (Equation 4). Consequently, this assures $\Delta\mu_i$ is always an energy gain.

$$\Delta\mu_i \leq 0 \text{ eV} \quad (4)$$

This upper bound on the free energies is referred to throughout the remaining text as the *rich* condition. Therefore given a rich supply of any elemental constituent its $\Delta\mu_i$ term is equal to zero. The rich condition serves as a universal reference point for all constituents and phases; beyond zero would imply a requirement of additional free energy from an unaccounted source.

3. Results and Discussions

Bismuth titanate of the pyrochlore structure ($\text{Bi}_2^{3+}\text{Ti}_2^{4+}\text{O}_7^{2-}$ abbrev. BTO), adopts Fd-3m space group symmetry that has international tables number 227 and Schoenfiles name OH-7

[60]. This face centered cubic symmetry has two origin choices that are either on cation-A or cation-B (note, A = Bi and B = Ti) [61]. Construction of BTO is described as alternate stacking of triple layers of TiO_6 octahedra and monolayers of $(\text{Bi}_2\text{O}_2)^{2+}$ units along the c-axis [62]. In Figure 1 a schematic view along a $\langle 111 \rangle$ direction of the cubic structure shows how $\text{O}'\text{Bi}_4$ tetrahedra interpenetrate corner connected TiO_6 octahedra in the pyrochlore structure. Experimental data consistently reports lattice parameters of BTO as, $a = 10.298 \text{ \AA}$ ($\alpha = \beta = \gamma = 90^\circ$) and the Ti-O, Bi-O, and Bi-O' bond lengths as 1.964, 2.559, and 2.227 $\text{\AA}$ respectively [40,45,63]. The distinction between O and O' atoms are based on their coordination with Bi atoms; O' atoms have shorter bond lengths with Bi and are responsible for the activity of Bi 6s lone pair electrons. Our DFT results were in good agreement with $a = 10.332 \text{ \AA}$ ($\alpha = \beta = \gamma = 90^\circ$) and Ti-O, Bi-O, and Bi-O' bond lengths at 1.982, 2.572, and 2.236 $\text{\AA}$ respectively. Our results also agree well with other theoretical results [61,64,65].

In Table 1 we show the structural properties for all three dopants $X = \text{Cr}$, Mn and Fe at the A and B sites. It can be seen from the lattice parameters that an overall cubic structure was retained in each case. The listed cell volumes however, show that dopants at the A-site had negligible effect on the cell's volume while dopants at the B-site caused considerable expansions. For Cr doping at the A-site (Cr_{Bi}), the Cr ion is mainly bonded to two O' atoms each with a bond length of 1.813 $\text{\AA}$, whereas the six O atoms surrounding the Cr ion were all 2.590 $\text{\AA}$ away. Compared to the Bi-O' bond length of pristine BTO (2.236 $\text{\AA}$), the $\text{Cr}_{\text{Bi}}\text{-O}'$ bond length was a reduction of about 19%; a significant reduction due to the smaller atomic size of Cr compared to Bi. However, the Ti-O bonds associated with this structure ranged from 1.893 to 2.086 $\text{\AA}$ (a mean of 1.978 $\text{\AA}$); a 0.2% reduction from that of pristine BTO (1.982 $\text{\AA}$). This shows that distortions from Bi substitutions can be compensated locally. On the other hand, for Cr

doping at the B-site (Cr_{Ti}), the Cr ion is bonded to six O atoms that each have a bond length of 1.954 Å. Compared to the Ti-O bond length of pristine BTO (1.982 Å), this is a reduction of about 1.5%. However, the Bi-O bonds associated with this structure ranged from 2.242 to 2.578 Å (a mean of 2.412 Å), so the Bi-O' bonds did not change much whereas the Bi-O bonds increased more than 4%. This shows that distortions caused by Ti-site doping are distributed over both cation sublattices. The trend is similar for Mn and Fe doping as well. For Mn_{Bi} the six O atoms surrounding the Mn atom are all 2.578 Å away and the two O' atoms have bond lengths of 1.793 Å, about a 20% reduction from pristine Bi-O' bond lengths. The Ti-O bonds in this structure ranged from 1.897 to 2.081 Å (a mean of 1.978 Å), about a 1% reduction from pristine Ti-O bond lengths. For Mn_{Ti} the six surrounding O atoms are 1.942 Å away. The Bi-O bonds associated with this structure ranged from 2.241 to 2.578 Å (a mean of 2.413 Å). Lastly, for Fe_{Bi} , the six surrounding O atoms are 2.598 Å away and the two O' atoms have bond lengths that are 1.813 Å. The Ti-O bonds associated with this structure range from 1.893 to 2.085 Å (a mean of 1.978 Å). For Fe_{Ti} the six surrounding O atoms have bond lengths that are 1.927 Å. The Bi-O bonds associated with this structure range from 2.242 to 2.578 Å (a mean of 2.411 Å).

To comprehensively correlate the structural properties to the nature of X doping in BTO, we have considered the stabilities of some dopant inspired phases (DIPs) and precursors of BTO in the context of free energy dependence. The following constrained equations represent free energy dependent formation of the secondary phases (precursors and DIPs) related to A-site transition metal doped BTO.

$$\Delta H_f^{X_{\text{Bi}}} = 7\Delta\mu_{\text{O}} + 2\Delta\mu_{\text{Ti}} + 1.875\Delta\mu_{\text{Bi}} + 0.125\Delta\mu_X \quad (5)$$

$$\Delta H_f^{X_{\text{Bi}}\text{O}_3} = 3\Delta\mu_{\text{O}}^{X_2\text{O}_3} + 2\Delta\mu_{\text{Bi}}^{X_{\text{Bi}}} \quad (6)$$

$$\Delta H_f^{X_{\text{Ti}}\text{O}_2} = 2\Delta\mu_{\text{O}}^{X_2\text{O}_3} + \Delta\mu_{\text{Ti}}^{X_{\text{Bi}}} \quad (7)$$

$$\Delta H_f^{BiXO_3} = 3\Delta\mu_O^{X_2O_3} + \Delta\mu_{Bi}^{X_{Bi}} + \Delta\mu_X \quad (8)$$

$$\Delta H_f^{XTiO_3} = 3\Delta\mu_O^{X_2O_3} + \Delta\mu_{Ti}^{X_{Ti}} + \Delta\mu_X \quad (9)$$

$$\Delta H_f^{X_2O_3} = 3\Delta\mu_O^{X_2O_3} + 2\Delta\mu_X \quad (10)$$

Equation 5 is the governing equation that generates the chemical potential landscape for X-doped BTO. Equations 6 and 7 represent formation of precursor oxides that could source Bi and Ti ions. Equations 8 and 9 represent formation of DIPs that are dependent on $\Delta\mu_{Bi}$ and $\Delta\mu_{Ti}$ and equation 10 represents formation of a DIP that is independent of $\Delta\mu_{Bi}$ and $\Delta\mu_{Ti}$. Each of these linear equations introduces further constraints on the chemical potentials that empower us to analyze the effects of free energy changes given any coupling condition. In experiment, coupling conditions can be considered in many different ways, however, for brevity we will only consider two different cases in this study. The two different cases we have examined are, (i) formation of a secondary phase coupled only with X doped BTO, and (ii) formation of a secondary phase coupled with X doped BTO and the other secondary phases. In Figure 2A), the chemical potential landscapes representing case (i) formation of the secondary phases is shown and the following inequalities represent the range of chemical potentials that avoid their formation. For case (i) formation, a simultaneous system of equations can be made out of Equations 5 and 6 (if we are considering simultaneous Bi_2O_3 formation). Then by imposing a constant X-rich condition and invoked the O rich and poor conditions ($\Delta\mu_O = 0$ and $\Delta\mu_O = \Delta\mu_{O,min}$, respectively). According to Equation 6, when $\Delta\mu_O = 0$ the value of $\Delta\mu_{Bi} = \Delta H_f^{Bi_2O_3}/2$, which is the Bi poor condition with respect to Bi_2O_3 . Now when $\Delta\mu_O = \Delta\mu_{O,min}$, we were simultaneously considering the Bi rich condition, $\Delta\mu_{Bi} = 0$ and according to Equation (6), $\Delta\mu_{O,min} = \Delta H_f^{Bi_2O_3}/3$ which is the O poor condition with respect to Bi_2O_3 . The unknown $\Delta\mu_{Ti}$ for O poor and O rich is then solved for by plugging the respective $\Delta\mu_{Bi}$ and $\Delta\mu_O$ pairs into Equation 5. In a similar fashion, the other

secondary phase boundaries were determined. Our calculated value for each formation enthalpy is given in Table 2 as a reference.

$$\sum_i n_i \Delta\mu_i < \Delta H_f^{Bi_2O_3} \quad (11)$$

$$\sum_i n_i \Delta\mu_i < \Delta H_f^{TiO_2} \quad (12)$$

$$\sum_i n_i \Delta\mu_i < \Delta H_f^{BiXO_3} \quad (13)$$

$$\sum_i n_i \Delta\mu_i < \Delta H_f^{XTiO_3} \quad (14)$$

$$\sum_i n_i \Delta\mu_i < \Delta H_f^{X_2O_3} \quad (15)$$

Apparently, case (i) formation does not allow single phase formation of X doped BTO, due to the fact each phase has its own range of $\Delta\mu_O$ which may not be suitable to form the other phases. According to our inequalities if a chemical potential is too low the referenced secondary phase cannot form. Take for example $\Delta\mu_{O,min} = \Delta H_f^{TiO_2}/2$, which equals -4.129 eV, at this O-poor condition, X-doped BTO itself cannot even form because $\Delta\mu_{O,min} = \Delta H_f^{XBi}/7$ is always greater than -4.129 eV (note Bi_2O_3 and TiO_2 boundary lines are parallel in each case).

Now for case (ii) formation we make a simultaneous system of equations out of Equations (5), (6) (that is considering the formation of Bi_2O_3 as an example again) and the equation that represents formation of the least stable secondary phase (e.g. the one that has the largest formation enthalpy). So, for $X = Cr$ or Mn , Equation 8 is considered and for $X = Fe$, Equation 10 is considered. In Figure 2B), the chemical potential landscapes representing case (ii) formation are shown. Notice how the Bi_2O_3 and TiO_2 boundary lines are now perpendicular in each case. According to the inequalities (Equations 11-15), single phase formation of X doped BTO emerges as the area bounded by $\Delta\mu_{O,min}$ and the $\Delta\mu_{Bi}/\Delta\mu_{Ti}$ axes (the shaded area). Choosing to define $\Delta\mu_{O,min}$ with respect to the least stable phase promotes formation of BTO and all secondary phases. It is worth mentioning here that only one independent DIP (X_2O_3) boundary is

shown while other independent DIP boundaries are not shown. This is due to the fact different binary X-oxides will not coexist in the same plane as defined in Figure 2B). For example, lines representing Mn_2O_3 , MnO_2 and BiMnO_3 cannot exist in the same plane where Mn-BTO is stable at thermodynamic equilibrium; Mn_2O_3 and BiMnO_3 will co-exist in one plane (as shown here) and MnO_2 and BiMnO_3 will exist in another plane (not shown here).

The case (ii) formation picture produces chemical potential landscapes that are easily correlated to experiment. For example, the small region in Figure 2B) where Bi_2O_3 and TiO_2 are coexistent with BTO, can be correlated to the chemical parameters of reference 54 where stable $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Bi}_2\text{Ti}_2\text{O}_7$ (note: $\text{Bi}_4\text{Ti}_3\text{O}_{12} = \text{Bi}_2\text{Ti}_2\text{O}_7 + \text{Bi}_2\text{O}_3 + \text{TiO}_2$) was formed. According to the authors, when the Cr wt. % was increased, the heterostructure became predominantly $\text{Bi}_2\text{Ti}_2\text{O}_7$. Correlating this observation with our DFT results, one can easily determine there is a free energy dependence between Cr and O ions. Since the pure phase zone is along the direction of reducing O free energy we can predict pure phase Cr-doped BTO should be done in O-poor conditions.

From Figure 2B, we chose the points **a**, **b**, and **c** because of their relationship to chemical parameters that can be controlled in experiment. Point **a** is the $\Delta\mu_{\text{Bi}}$ -intercept which happens to also be the Ti-rich triple point; three Ti-related secondary phases converge to this point. Point **b** is the $\Delta\mu_{\text{Ti}}$ -intercept/Bi-rich triple point and point **c** has coordinates in the $(\Delta\mu_{\text{Bi}}, \Delta\mu_{\text{Ti}})$ -plane equal to $(-2.5, -1.25)$. This coordinate pair was taken to represent a Bi/Ti ratio less than 1, as A-site doping is more stable than B-site doping in general according to our formation enthalpy calculations (not shown here explicitly). Figure 2C) shows the formation energies of first and second order X doping configurations with respect to points **a**, **b** and **c**; the linear expression for defect formation energy is given by Equation 2. The first order configurations are, for example, substitutions of A and B cations or X_{Bi} and X_{Ti} , respectively. The second types are second order

configurations defined as X_{Bi} or X_{Ti} coupled with an O vacancy or interstitial ($X_{\text{Bi}}\text{-O}_{\text{vac}}/\text{O}_{\text{int}}$ and $X_{\text{Ti}}\text{-O}_{\text{vac}}/\text{O}_{\text{int}}$). Positive formation energies indicate endothermic reactions that require an input of energy and thus are less likely to form. Negative formation energies indicate exothermic reactions that form spontaneously and thus are more likely to form. At first glance it can be seen that A-site doping are exothermic reactions while B-site doping are endothermic reactions with respect to points **a** and **c**. At point **b**, A and B-site doping transition to endothermic and exothermic reactions respectively. Hence, only when the Ti condition is its poorest does X_{Ti} doping become favorable in comparison to X_{Bi} doping.

From our formation enthalpy calculations the most favorable doping configurations for $X = \text{Cr, Mn and Fe}$ are $X_{\text{Bi}}\text{-O}_{\text{vac}}$, $X_{\text{Bi}}\text{-O}_{\text{int}}$, and X_{Bi} , respectively. These are also the most favorable doping configurations with respect to points **a** and **c** of our chemical potential landscapes. Likewise, the least favorable doping configuration in terms of formation enthalpy is $X_{\text{Ti}}\text{-O}_{\text{int}}$ for all dopants, which happens to be the most favored doping configuration for all dopants at point **b**. This suggests X_{Ti} and O_{int} related doping, which are promoted in Ti-poor and O-rich conditions, correspond to formations of secondary phases.

In Figure 3, the charge density difference plots, $\Delta\rho_{\text{AB}}$, for pristine BTO and $X = \text{Cr, Mn, and Fe}$ doped BTO in A and B-sites are given. It can be seen from the A-site doping that the central dopant atom increases its orbital overlap with O' atoms and reduces its ionic components with O atoms, as Table 1 suggests. From the B-site doping column not much orbital overlap can be seen except in the Fe doping case where the overall bonding polyhedra gets smaller. Summarily, X_{Bi} doping configurations demonstrated the least amount of distortions in comparison to X_{Ti} doping configurations. The associated Ti-O and Bi-O bonds were virtually unchanged, but in the X_{Bi} cases X-O' was always a reduction in comparison to the Bi-O' bonds

of pristine BTO. As was pointed out in the X_{Bi} case, the A-site is a ‘distortion-tolerate site’ because of its bonding with the O’ atoms which are not shared with Ti atoms. Hence, for X_{Bi} the distortion is mainly along X-O’ bonds. On the other hand, Ti atoms are bonded with O atoms which are also shared by Bi atoms, so distortions at this site effect both sublattices.

In Figure 4 we show the electronic structures of A) pristine BTO, B) $\text{Cr}_{\text{Bi}}\text{-O}_{\text{vac}}$, C) $\text{Mn}_{\text{Bi}}\text{-O}_{\text{int}}$ and D) Fe_{Bi} which are the most favorable conditions with respect to point **c** of the chemical potential landscapes. In Figure 4(A), the electronic structure shows that Bi 6s lone pairs form an antibonding state with O’ 2p electrons at the VBM. The band gap is approximately 2.6 eV direct at the Γ -point. Deeper in the valence bands (not shown), the Bi 6s + O’ 2p bonding state pushes the valence band closer to the CBM. The CBM at the Γ -point shows a dispersive electronic state that is indicative of electrons with reduced effective mass in the first brillouin zone.

In Figure 4(B), the spin polarized, GGA calculated electronic structure of $\text{Cr}_{\text{Bi}}\text{-O}_{\text{vac}}$ is shown. The band structure shows both occupied and unoccupied mid gap bands that are virtually dispersion-less in the majority channel. Irrespective to these mid gap states the band gap is about 2.5 eV at the Γ -point. The PDOS shows that these mid gap bands have both Cr 2p and Cr 3d character but the 3d character is more dominant. The highest occupied mid gap state also has Ti 3d character which suggest some cation-cation interactions. This may be due to the fact, O’ states are reduced, given an O_{vac} . In the minority channel the band gap measured from the VBM to the one unoccupied mid gap band is about 2.3 eV at the Γ -point and measured to the CBM it is 2.5 eV. The PDOS shows that the unoccupied mid gap band is mostly composed of Cr and O’ 2p levels.

In reference 54, the authors discuss their Cr 2p fine XPS spectra, and based on the difference between their observed binding energy (576.3 eV) and a reported [66] Cr^{3+} binding

energy (577.6 eV), they suggest at the low Cr concentrations they considered, Cr ions have predominantly 4+ charge states and therefore sit at Ti-sites. In an experimental study of the XPS spectra of first row transition metals, a controversy between binding energies of Cr^{3+} and Cr^{4+} [67] is discussed. It was stated that, due to the overlapping of fine multiplet Cr^{3+} spectra with singlet Cr^{6+} spectra, false readings for Cr^{4+} are common. Furthermore, authors from another experimental study on the photo-reduction of hexavalent Cr by XPS measurements found the fitting parameters for Cr^{3+} and Cr^{4+} to be 576.3 eV and 575.2 eV, respectively [68], therefore the experimental determination is very illusive. From our results, shown in Table 1, X_{Ti} doping corresponds to a slight increase in the lattice parameters whereas X_{Bi} doping corresponds to little or no change in the lattice parameter. Therefore one can expect the characteristic XRD peaks of X-doped BTO to either shift to lower angles in the case of X_{Ti} doping or remain the same in the case of X_{Bi} doping. In Fig. 1, of reference 58, the characteristic XRD peaks of the assumed Cr_{Ti} doping virtually stay the same with increasing Cr doping and in Fig 3 of reference 54, the characteristic XRD peaks shifted to higher angles.

In Figure 4C), the spin polarized, GGA calculated electronic structure of $\text{Mn}_{\text{Bi}}\text{-O}_{\text{int}}$ is shown. The band structure of the majority channel shows both occupied and unoccupied mid gap bands composed of Mn 3d + O' 2p. However, due to their dominant 3d character, they are very flat which indicates effective hole masses would be too massive for enhanced photoconduction. Nonetheless, the band gap measured from the VBM to the CBM between the Γ - and L-points is about 2.3 eV. In the minority channel the band gap is about 2.1 eV measured from the one occupied mid gap band to the CBM between the Γ - and L-points. From the VBM to CBM the band gap is about 2.3 eV. The PDOS shows that the composition of the VBM and the occupied

mid gap state are mostly O'2p. This may be due to the fact more O' 2p states are available, given an O_{int}.

In Figure 4D), the spin polarized, GGA calculated electronic structure of Fe_{Bi} is shown. In the band structure for the majority channel, mid gap states are absent and the band gap is about 2.3 eV, direct at the Γ point. The VBM is predominantly O' 2p-like, and the CBM is Ti 3d-like. In the minority channel there resides five unoccupied mid gap bands. Irrespective to these mid gap bands the band gap is about 2.5 eV.

4. Conclusions

We have systematically studied the nature of X = Cr, Mn, and Fe doping in BTO. Evidently, incorporation of these 3d transition metals in BTO increases its visible light absorption. The band gap of BTO was reduced on average by 0.3 eV upon X doping. Substitutions in the A-sites are energetically favored compared to substitutions in the B-sites. Depending on occupation of the 3d levels, O vacancies or interstitials accompany the doping. X_{Ti} related doping configurations in general had positive formation energies with respect to the single phase stability zone. The X_{Ti}-O_{int} doping configuration was the most favorable with respect to Ti-poor/Bi-rich conditions in each case. As these defects are unstable, they can be associated with formations of secondary phases. With respect to the experimental evidence, our results showing Cr_{Bi}-O_{vac} to be the most favored doping configuration, suggested Cr ions have charge states that are predominantly 3+ in BTO, which supports our prediction of B-site substitutions being more stable. Mn_{Bi}-O_{int} as a the most favored configuration suggest Mn ions are most likely in a 4+ charge state which would require a coordination change with O atoms in the A-site. Fe_{Bi} as the most favored doping configuration in BTO suggested Fe ions are most likely in a 3+ charge state. Ti-poor conditions are associated with formations of secondary

phases. The favorable X doping configurations all had some common features which may be responsible for increasing photocurrent. For example, each favorable doping configuration preserved cubic symmetry. The flexibility of O'-Bi-O' chains were used to compensate local distortions. TiO_6 octahedra remained rigid, by not changing their coordination with O atoms.

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Figure 1: Schematic view of BTO dual type polyhedra along a $\langle 111 \rangle$ direction. The large, purple atoms are Bi atoms, the smaller, bluish atoms are Ti atoms, and the smallest red atoms are O atoms. The shaded regions of the structure are TiO_6 octahedral units while the un-shaded regions are the $\text{O}'\text{Bi}_4$ tetrahedral units. Bi-O bonds are not shown.

Table 1: Cell parameters ($\text{\AA}$), lattice angles (degrees), cell volume ($\text{\AA}^3$), and mean bond lengths ($\text{\AA}$) for dopants $X = \text{Cr, Mn or Fe}$ in pristine BTO at the A and B cation sites.

<i>Species</i>	a	α	B	γ	V	Bi-O	Ti-O	X-O
BTO	10.330	90.000	90.000	90.000	1102.156	2.486	1.982	
Cr_{Bi}	10.328	89.933	90.067	90.067	1101.610	2.440	1.978	1.813
Cr_{Ti}	10.348	89.881	90.119	90.119	1108.065	2.412	1.982	1.954
Mn_{Bi}	10.324	89.907	90.093	90.093	1100.421	2.439	1.978	1.793
Mn_{Ti}	10.347	89.868	90.132	90.132	1107.792	2.413	1.982	1.942
Fe_{Bi}	10.327	89.948	90.053	90.053	1101.471	2.441	1.978	1.813
Fe_{Ti}	10.345	89.875	90.125	90.125	1106.961	2.411	1.982	1.928

Figure 2: Stability analysis of X = Cr, Mn and Fe doping in BTO. A.) are the chemical potential landscapes that represent case (i) formation of secondary phases. B.) are the chemical potential landscapes that represent case (ii) formation of secondary phases and C.) are the defect formation energy distributions with respect to the points **a** = the $\Delta\mu_{Bi}$ -intercept or Ti-rich triple point, **b** = $\Delta\mu_{Ti}$ -intercept or Bi-rich triple point, and **c** = (-2.50,-1.25) of the corresponding chemical potential landscape. All scales are in eV.

Table 2: Calculated formation energies in eV. For each dopant $X = \text{Cr, Mn, Fe}$, the A-site substitution is shown as it is the most stable substitution site for all dopants. Bismuth oxide and titanium dioxide are the dopant independent secondary phases considered. Other phases are dopant and Bi/Ti dependent secondary phases and dopant Bi/Ti independent phases. For $X = \text{Cr}$ and Mn , BiXO_3 has the highest formation energy and for $X = \text{Fe}$, X_2O_3 has the highest formation enthalpy.

<i>Phase</i>	X=Cr	X=Mn	X=Fe
X_{Bi}	-24.050	-23.900	-23.998
Bi_2O_3	-10.074	-10.074	-10.074
TiO_2	-8.258	-8.258	-8.258
BiXO_3	-6.845	-6.510	-8.455
XTiO_3	-11.941	-11.428	-10.761
X_2O_3	-9.726	-8.773	-6.072

Figure 3: Charge density differences for A and B cation sites with A) pristine BTO, B) Cr-BTO, C) Mn-BTO, and D) Fe-BTO. The isosurface levels are the same value in each case. Fe shows a significant orbital overlap in comparison to Cr and Mn

Figure 4: GGA determined electronic structures for the most favorable X doping configurations per the free energy landscape. A) BTO, B) $\text{CrBi-O}_{\text{vac}}$, C) $\text{MnBi-O}_{\text{int}}$, and D) FeBi . FCC Brillouin zone was used to specify symmetric points in the lattice. The left panel represents the majority channel and the right panel (if shown) represents the minority channel. The center panels are the site projected partial density of states.