

Rebuttal to “density functional theory investigation of site prediction of Fe substitution in barium titanate”

Abstract

Through this letter to the editor (Rebuttal), we had given our explanation for the queries raised by Professor Juan J. Meléndez commenting on the high substitution energies, the small simulation supercells, and the inconsistency of experimental data and simulation results. We agree with the comment that applying a “chemical potential diagram” is a general way to study defect system. However, there are some experimental concerns on “what the initial materials should be used”, whereas many degrees of freedom become feasible. Therefore, the formation energy equation (with foreign atoms substitution) cannot be trivially answered by the formation energy within a chemical potential diagram framework, unlike substitution energy calculated directly from our suggested chemical equation. We explain in the details on our approach and confirm the validity of our main equation; $\text{FeO} + \text{Ba}_8\text{Ti}_8\text{O}_{23} \rightarrow \text{Ba}_8\text{Ti}_7\text{FeO}_{23} + \text{TiO}_2$ for the substitution energy with $2 \times 2 \times 2$ supercell size which the results still show some suggestive trends.

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1. Comments on the paper entitled “Density functional theory investigation of site prediction of Fe substitution in barium titanate” [Ceramics International 39 (2013), 293–296] by Juan J. Meléndez.

Several physical inconsistencies in this paper were found. First, the authors report unrealistically high (and therefore incorrect) substitution energies. These values arise because the chemical potentials of the species involved are not taken into account in their definition of substitution energy; small contributions may also arise from the use of too small simulation supercells. Secondly, the trends shown by the results does contradict the evidence that iron incorporates to barium titanate mostly as Fe(III). Finally, the authors find iron-doped barium titanate to exhibit a metallic character, which is clearly inconsistent with experimental data and simulation results. Some suggestions to get much more realistic results were given.

In their interesting paper [1], Nimmanpipug and co-workers use the DFT formalism within the LDA approximation to elucidate the most favorable mechanism for incorporation of iron to the lattice of tetragonal barium titanate. For the valence charges +2 and +3, the authors place the dopant at the host barium and titanium sites [for Fe(II)] or the titanium one [for Fe(III)], create the proper charge-compensating defects (oxygen

vacancies) and study the variation of the substitution energy with the relative positions of the dopants and the oxygen vacancies. Their results are listed in Tables 1 and 2 of Ref. [1]. In addition, the authors investigate the effect of the incorporation configuration on the band structure and density of states of the system. In my opinion, DFT is indeed one of the possible right frameworks to deal with this problem, since electronic effects are greatly involved in the defect structure of solids [2]. However, the authors' results do not seem to be correct for a number of reasons:

The authors do not use the right definition of the substitution energies. Let us consider, for instance, the incorporation of Fe (II) to the titanium site with compensation by an oxygen vacancy, which may be described by the Kröger–Vink equation:



The authors calculate the substitution energy as

$$E_{\text{sub}} = E(\text{Fe}_{\text{Ti}}) + E(\nu_{\text{o}}) + E(\text{TiO}_2) - E(\text{FeO}) \quad (2)$$

Where $E(a)$ seems to hold for the energy per atom of configuration a . This expression yields unrealistic values of about 119 eV (in absolute value) as listed in Table 2 of Ref. [1]. It is relatively easy to realize that Eq. (2) is actually wrong. Indeed, the effect of the last term in the right-side member is to

counter balance the appearing of a “strange” iron atom in a lattice which otherwise will contain only titanium, barium and oxygen in their respective positions. But the iron atom included in the defective barium titanate lattice has a chemical environment which is different than that in FeO and, therefore, such a correction does not suffice. Please note that Eq. (2) would be applicable, however, within a semi-classical formalism (i.e., molecular dynamics), where electronic effects are not explicitly taken into account.

The defect substitution energy, assuming the defect to be neutral, is instead calculated according to

$$E_{sub} = E(\text{defect}) - E(\text{pure}) - \sum_i n_i \mu_i \quad (3)$$

where $E(\text{defect})$ and $E(\text{pure})$ are, respectively, the energies of the defective and defect free supercells, n_i is the number of atoms of defective species which have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell when the defect has been created, and is the chemical potential of the species i , which accounts for the particular chemical environment within the lattice [3].

The authors use a very small simulation supercell. In a supercell framework, which assumes periodic boundary conditions to hold in all directions, it is well known that dopants interact with their periodic images, much more markedly if they are charged, and such spurious interactions may well alter the results of substitution energies. Since the computational resources available may be limited, one should use simulation supercells of increasing size until the energies are calculated within a prefixed tolerance. $2 \times 2 \times 2$ Supercells, like those used by the authors, have been found to be small in barium titanate and similar systems [4]; $3 \times 3 \times 3$ ones, instead, are reasonably accurate. One could also rescale the results with the size of the simulation supercell. Indeed, the images of neutral defects interact mainly elastically, and the corrections to the energy scale as V^{-1} (being V the volume of the supercell); for charged defects, the corrections vary as $V^{-1/3}$ instead [5,6]. The authors could run simulations using $3 \times 3 \times 3$ cells or, alternatively, using cells of different volumes and fit their results to the appropriate scaling law.

Apart from the previous, and assuming that the results show the right trend (although not the right values), the authors' results are inconsistent with the almost unanimous evidence that iron incorporates as Fe(III) to barium titanate [7–10]; valence changes seem to occur only after thermal treatments [10,11]. In any case, the differences of energy between valence charges are not large, which explains why the incorporation mechanism may be so sensitive to the thermodynamic (i.e., oxygen partial pressure) or stoichiometric (i.e., Ba/Ti molar ratio) conditions under some circumstances. I do not think that energy differences of the order of 30 eV or more may be physically justifiable.

The authors build the band structure of two defective systems [Fe(II) and Fe(III) in their most probable configurations] as well as the corresponding densities of states (*cf.* Fig. 2 of Ref. [1]). In both cases, the Fermi level lies within an energy band instead of within the gap. In other words, the authors predict Fe-doped barium titanate to be a metal, contrarily to the

wide evidence of its insulating character [see, for instance, [12] and references therein]. This is obviously not related to the wrong definition of substitution energy, but to a limitation of DFT itself. Indeed, when atoms with partially filled d shells are present, standard DFT is known to delocalize the inner electrons much more than they actually are, which makes a fake metallic character to appear. This may be solved by using the exact exchange (EXX) approximation, although its application to solids is extremely costly from the computational point of view. Alternatively, one may adopt the so-called DFT+U formalism [13,14], in which an extra term penalizing the occupations of the d shells to be non-integer is added to the energy functional; this is much more less computationally expensive and, under some circumstances, may be derived from first-principles [15]. Iron atoms have unfilled inner d shells and, therefore, the DFT+U formalism should be useful. The forced localization of the inner electrons is likely to give rise to the energy gap which is experimentally observed. An additional issue is that, because of the existence of the incomplete d shells, the spin-polarized LDA should be used; please note that the authors do not provide any information on this respect.

Iron-doped cubic barium titanate has been the subject of a recent paper [16] which uses the DFT formalism within the GGA+U approximation. Using $3 \times 3 \times 3$ simulation supercells, the authors use Eq. (3) and report that Fe(II) incorporation within barium titanate yields energies of the order of 3 eV for a number of mechanisms, except for a few quite unlikely cases which involve the creation of the very energetic titanium vacancies. Energies of this order are much more realistic than the abnormally high negative values reported by Nimmanpipug and co-workers. The most stable mode is found to be acceptor incorporation of Fe(III) at two titanium sites with the creation of an oxygen vacancy, but the most important, which agrees well with the experimental evidence. In addition, the density of states of both pure and iron-doped barium titanate exhibit a gap, within which the Fermi level lies, consistently with the insulating behavior of these systems.

2. Rebuttal

Through this rebuttal, we would like to give our explanation in the section accordingly for the queries/comments raised by Prof. Juan J. Meléndez on our published paper “Density functional theory investigation of site prediction of Fe substitution in barium titanate [Ceramics International 39 (2013), 293–296]”.

The substitution energy depends upon the chemical potential of relevant species in the reservoir. All possibility of dopants composing of Fe(II) and Fe(III) substituting in barium titanate based on typical synthesis process were carried out. Since the purpose of this work is to provide additional information for the general view of how the impurity in the form of Fe(II) and Fe(III) incorporates into the tetragonal BaTiO₃, we therefore initially define where each applicable oxidation state of Fe should technically come from. Specifically, we have carried this out by employing FeO and Fe₂O₃ as the source for Fe(II)

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