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Density functional theory investigation of site predilection of Fe substitution in barium titanate

Piyarat Nimmanpipug[a,b,*], Aroon Saelor[a], Laongnuan Srisombat[a,b], Vannajan Sanghiran Lee[a,b,c], Yongyut Laosiritaworn[b]

[a]*Computational Simulation and Modelling Laboratory (CSML), Department of Chemistry, Faculty of Science, Chiang Mai University, 239 Huay Kaew Road, Chiang Mai 50200, Thailand*

[b]*Thailand Center of Excellence in Physics, Commission on Higher Education, 328 Sri Ayutthaya Road, Bangkok 10400, Thailand*

[c]*Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia*

Abstract

The site predilection and effects of the impurity in the form of Fe (II) and Fe (III) in the tetragonal barium titanate lattice were systematically determined by density function theory calculations. All electron calculation was carried out in the local density approximation (LDA). It is shown that both Fe (II) and Fe (III) prefer to substitute at the titanium site with oxygen vacancy compensation as a result of lowest substitution energy. Effect of Fe dopant both in form of Fe (II) and Fe (III) at titanium site with oxygen vacancy compensation lead to change in electrical property in terms of energy band structure of the tetragonal barium titanate lattice.

Keywords: B. Impurities; D. $BaTiO_3$; D. Perovskites

1. Introduction

Barium titanate ($BaTiO_3$) with perovskite ABO_3 structure has been extensively studied because of its interesting electrical properties for instance, ferroelectricity and piezoelectricity. According to a number of research works, properties of this material can be modified to achieve a variety of character depending on the phase diversity, in particular, the addition of appropriate dopant, e.g. iron [1–5].

To clarify the material's properties from an atomistic level, density function theory calculations have been utilized in various aspects [6–10]. Both local density approximation (LDA) method and generalized gradient approximation (GGA) method were widely applied to study the properties of ABO_3-type perovskites.

In this study, simulation techniques will be used for position determination of dopant that substitute in structure. The influence of dopant impurity ions on band structure and density of state will be predicted.

2. Calculation methodology

In this work, all calculations were performed using the density functional theory in *Dmol3* program [11–13]. The perovskite structure of barium titanate is in a P4mmm space group tetragonal crystal with lattice parameters of $a=b=3.997$ Å, $c=4.033$ Å [14,15]. Atomic structure containing Fe impurity was simulated in a $Ba_8Ti_8O_{24}$ supercell of $8.00 \times 8.00 \times 8.06$ Å^3 in periodic condition as depicted in Fig. 1. The position of Fe (II) and Fe (III) are systematically assigned until the configuration with minimum substitution energy is achieved. The Kohn–Sham equations are solved using the functional of Perdew and Wang [16] in LDA scheme. Double Numerical plus *d*-functions (DND) basis set corresponding to each atomic orbital was used. The Brillouin zone was sampled with a

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[*] Corresponding author at: Computational Simulation and Modelling Laboratory (CSML), Department of Chemistry, Faculty of Science, Chiang Mai University, 239 Huay Kaew Road, Chiang Mai 50200, Thailand. Tel.: +66 53943341; fax: +66 53892277.

E-mail address: piyaratn@gmail.com (P. Nimmanpipug).

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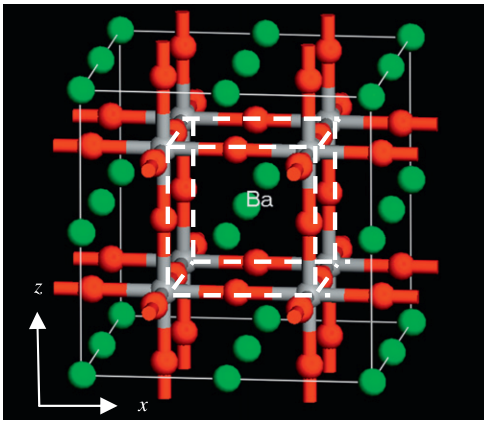

Fig. 1. Structure of barium titanate model ($Ba_8Ti_8O_{24}$).

$2 \times 2 \times 2$ irreducible Monkhorst-Pack *k*-point grid for structural relaxation and for the electronic density of states with a spatial resolution of 0.5 nm^{-1}. An orbital cutoff of 5.2 Å was used for all atoms, and the convergence threshold for calculation of the self-consistent energy was 10^{-5} Ha.

It is possible for dopants comprising of Fe (II) and Fe (III) to substitute in either barium or titanium sites but each possible structure has a different substitution energy. For divalence dopant, Fe (II) can substitute either barium sites or titanium sites. For substitution at barium sites no charge compensating defect is required, whereas substitution at the titanium site is compensated by formation of oxygen vacancies to maintain electro neutrality. Kroger–Vink notation was used in the reactions depicted

$$\mathrm{FeO} + \mathrm{Ba}_{\mathrm{Ba}} \rightarrow \mathrm{Fe}_{\mathrm{Ba}} + \mathrm{BaO}$$

$$\mathrm{FeO} + \mathrm{Ti}_{\mathrm{Ti}} + \mathrm{O}_{\mathrm{O}} \rightarrow \mathrm{Fe}_{\mathrm{Ti}} + \mathrm{V}_{\mathrm{O}} + \mathrm{TiO}_2$$

As barium titanate is tetragonal in structure, so oxygen vacancies have two possible structure, i.e. horizon oxygen vacancy and vertical oxygen vacancy.

In case of trivalence dopant (Fe (III)), there are two different substitution models. The first model is substitution at the barium site where excess negative charge is compensating the titanium vacancy. The second model is a substitution at the titanium site, where the excess negative charge is compensated by oxygen vacancy

$$\mathrm{Fe_2O_3} + 4\mathrm{Ba}_{\mathrm{Ba}} + \mathrm{Ti}_{\mathrm{Ti}} \rightarrow 4\mathrm{Fe}_{\mathrm{Ba}} + \mathrm{V}_{\mathrm{Ti}} + 3\mathrm{BaO} + \mathrm{BaTiO_3}$$

$$\mathrm{Fe_2O_3} + 2\mathrm{Ti}_{\mathrm{Ti}} + \mathrm{O}_{\mathrm{O}} \rightarrow 2\mathrm{Fe}_{\mathrm{Ti}} + \mathrm{Vo} + 2\mathrm{TiO_2}$$

Table 1
Fe (II) substitution site: oxygen vacancy, and substitution energy.

Substitution site	Oxygen vacancy	Lattice parameters (Å)			Substitution energy (eV)
		a	*b*	*c*	
Barium	–	4.000	4.000	4.020	−5.19013
Titanium	(0,0,2/1)	4.000	4.000	4.031	−119.176
Titanium	(0,1,2/1)	3.999	3.999	4.030	−119.179
Titanium	(1,1,2/1)	4.000	4.000	4.031	−119.178
Titanium	(2/1,0,0)	4.000	4.000	4.030	−119.178
Titanium	(1,2/1,0)	4.001	4.001	4.030	−119.178
Titanium	(2/1,0,1)	4.000	4.000	4.030	−118.637
Titanium	(1,2/1,1)	4.000	4.000	4.030	−119.519

Table 2
Fe (III) substitution site: titanium substitution coordinate and its substitution energy.

Substitution site	Oxygen vacancy	Lattice parameters (Å)			Substitution energy (eV)
		a	*b*	*c*	
(0,0,0) (1,0,0)	(1/2,0,0)	3.900	3.900	4.022	−83.1683
	(0,1/2,0)	3.890	3.890	4.020	−83.2552
	(1,1,1/2)	3.986	3.986	4.019	−83.2552
	(1/2,0,1)	4.021	4.020	4.186	−83.2552
	(0, 1/2,1)	3.985	3.985	4.047	−83.2553
	(1/2,1,1)	3.999	4.000	4.019	−83.2551
	(1,0, 1/2)	3.997	3.998	4.056	−83.2551
	(0,1,1/2)	3.999	4.000	4.045	−83.2546
(0,0,0) (0,1,1)	(1/2,0,0)	4.000	4.000	4.020	−83.2547
	(1/2,0,1)	4.000	4.000	4.024	−83.2547
	(0,0, 1/2)	4.000	3.999	4.030	−83.2186
	(1,0, 1/2)	4.000	4.000	4.020	−83.2547
(0,0,0) (0,0,1)	(0,0, 1/2)	4.000	4.000	4.032	−83.2547
	(1,0, 1/2)	4.000	4.000	4.020	−83.2547
	(1,1, 1/2)	4.000	4.000	4.023	−86.4220
	(1/2,0,0)	4.000	4.000	4.030	−83.2547
	(1, 1/2,0)	3.998	3.999	4.041	−83.2547
(0,0,0) (1,0,1)	(0,0, 1/2)	4.001	4.000	4.035	−83.2548
	(1,1, 1/2)	4.002	4.003	4.037	−83.2547
	(1, 1/2,0)	4.000	4.001	4.020	−83.2546
	(1/2,0,0)	4.002	4.001	4.038	−83.2582
	(1/2,1,0)	3.998	3.999	4.040	−83.2565
(0,0,0) (1,1,1)	(1/2,0,0)	4.000	4.000	4.035	−83.2565
	(1, 1/2,0)	4.000	4.000	4.030	−83.2546
	(0,0, 1/2)	4.000	3.999	4.030	−83.2546
	(1,0, 1/2)	4.000	4.010	4.032	−83.2546

3. Results and discussion

3.1. Fe (II) and Fe (III) substitution site location

In this section, calculated substitution energy (E_{sub}) for the iron oxide in the barium titanate lattice was reported. A series of Fe ions substitutions in the perovskite lattice depending on the charge compensation defect lead to different substitution energy. Foreign Fe^{2+} ion in the perrovskite introduces different substitution energy as shown in Table 1. Fe (II) substituted at titanium site and oxygen vacancy at (1,1/2,1) compensation is lowest substitution energy structure. Note that in this case, E_{sub} will be calculated as follows:

$$E_{\mathrm{sub}} = E(\mathrm{Fe}_{\mathrm{Ti}}) + E(\mathrm{V}_{\mathrm{O}}) + E(\mathrm{TiO}_2) - E(\mathrm{FeO})$$

In the case of Fe (III), the relation between various ways of substitution with substitution energy was depicted in

Table 2. For this case, E_{sub} will be calculated as shown below

$$E_{\mathrm{sub}} = 1/4(4E(\mathrm{Fe_{Ba}}) + E(\mathrm{V_{Ti}}) + E(\mathrm{BaTiO_3}) + 3E(\mathrm{BaO}) - 2E(\mathrm{Fe_2O_3}))$$

According to the obtained result, the most probable structure is Fe (III) substituted at two positions titanium site ((**0**,**0**,**0**) and (0,0,1)) and oxygen vacancy at coordination of (**1**,1,1/2).

3.2. Energy band structure and density of state

Brillouin zone of the tetragonal lattice with path: Γ–X–M–Γ–Z–R–A–Z|X–R|M–A was used in band structure and density of state calculation as shown in Fig. 2. Energy band structure profile was found slightly change due to oxidation state and substitution site predilection. The most probable structures of Fe (II) and Fe (III) doped barium titanate was selected from the previous section. In this calculation, Fe (II) and Fe (III) doped structure show energy gap of 1.41 and 0.81 eV, respectively.

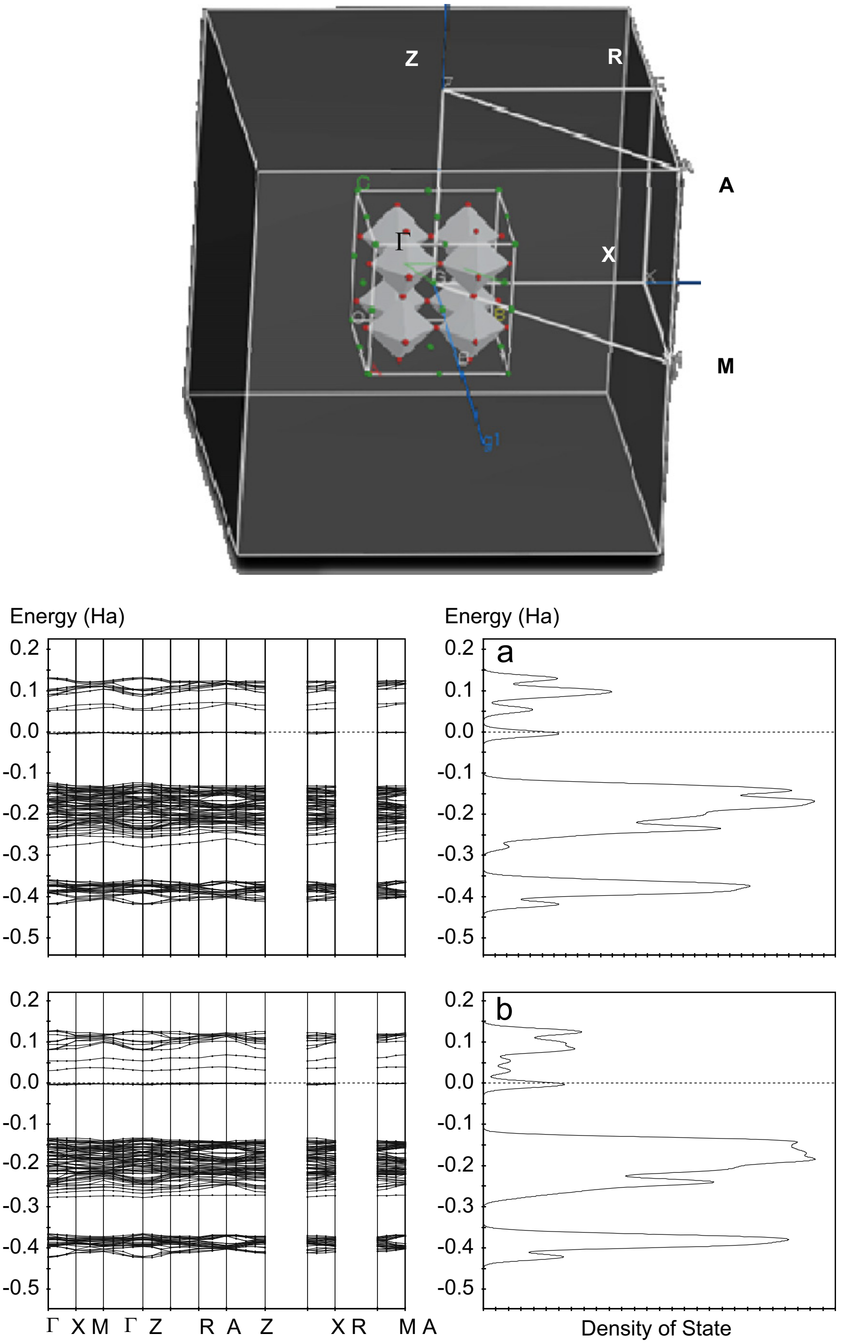

Fig. 2. Brillouin zone, path, energy band structure and density of states of (a) Fe (II) doped (b) Fe (III) doped barium titanate.

4. Conclusion

The effects of the impurity in the form of Fe (II) and Fe (III) in the tetragonal barium titanate lattice were systematically investigated by the calculation based on density function theory.

All electron calculation was carried out in the local density approximation. It is shown that both Fe (II) and Fe (III) prefer to substitute at the titanium site with oxygen vacancy compensation as shown in lower substitution energy. Slight deviation in lattice parameters was remarked upon in the study. Effect of Fe dopant both in form of Fe (II) and Fe (III) at titanium site with oxygen vacancy compensation lead to a change in electrical conductivity of the tetragonal barium titanate lattice. Fe (II) substituted at titanium site with oxygen vacancy compensation at (1,1/2,1) and Fe (III) substituted at two positions titanium site ((0,0,0) and (0,0,1)) with oxygen vacancy at (1,1,1/2) were suggested.

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