

## Effect of interstitial hydrogen on structural and electronic properties of BaTiO<sub>3</sub>

ARVIDS STASHANS† and JOHNNY CHIMBORAZO

Centro de Investigación en Física de la Materia Condensada, Corporación de Física, Fundamental y Aplicada, Apartado 17-12-637, Quito, Ecuador

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### ABSTRACT

We investigate the geometry and electronic structure of an interstitial H atom in the BaTiO<sub>3</sub> crystal considering both cubic and tetragonal crystallographic lattices. A quantum-chemical method based on the Hartree–Fock formalism is used throughout the study. Interstitial H is found to bind to one of the O atoms, forming the so-called OH group. At equilibrium, the O–H distances are found to be 0.89 and 0.91 Å for cubic and tetragonal lattices respectively. The performed automated geometry optimization procedure of the defective region shows considerable outward movements of atoms closest to the impurity. The role of the H impurity in ferroelectric polarization in the BaTiO<sub>3</sub> crystal is analysed using the results obtained in connection with the available experimental data on ferroelectric perovskites.

### § 1. INTRODUCTION

The perovskites are an extremely important class of ceramic materials which are now the focus of extensive study. Because of its large electro-optic coefficients and high photorefractive sensitivity (Feinberg *et al.* 1980), BaTiO<sub>3</sub> is of special interest. Knowledge of the specific features of possible defects in a photorefractive compound is necessary in order to optimize the performance of the material, such as speed and maximum refractive index changes. This material also exhibits ferroelectric and piezoelectric properties and therefore finds increasing processibility as an active element in microelectronic devices. Additionally, BaTiO<sub>3</sub> is a promising material for self-pumped phase conjugation or holographic storage (Krätzig *et al.* 1980, Feinberg 1982) and inexpensive diode lasers (Rytz *et al.* 1990).

It is known that the main properties of perovskite crystals are strongly influenced by the presence of point defects. H is a ubiquitous impurity and its role in structural and electronic properties of BaTiO<sub>3</sub> is not yet elucidated sufficiently. An important issue concerning the H impurity in BaTiO<sub>3</sub> is its effect on the ferroelectric polarization. When ferroelectrics are used in conjunction with Si, H contamination during Si passivation can result in a loss of ferroelectricity. However, results from a number of experiments indicate that a main source of degradation (Zafar *et al.* 1997, Ikarashi 1998, Kushida-Abdelghafar *et al.* 1999) is H-induced chemical changes at metal–oxide interfaces. It has also been suggested that H can induce the loss of bulk

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† Email: sauleskalns@yahoo.com

ferroelectricity in perovskite ferroelectrics where O loss at the interface is not significant (Aggarwal *et al.* 1998). Despite numerous studies on the H impurity in ferroelectric BaTiO<sub>3</sub> and PbTiO<sub>3</sub> crystals, no clear understanding of the theoretical basis of H-atom behaviour in these materials exists. Thus the main purpose of our research is to find equilibrium positions of the H atom in cubic and tetragonal lattices of the BaTiO<sub>3</sub> crystal and to discover possible impurity-atom effects upon the electronic structure of the crystal and, furthermore, its influence on ferroelectricity in the tetragonal phase of the BaTiO<sub>3</sub> crystal.

In our studies we have chosen to use the intermediate neglect of differential overlap approach developed especially for periodic systems, for example crystal studies. Our method as implemented in the CLUSTERD computer code (Stefanovich *et al.* 1990) is based on a strict and reliable parametrization scheme (Shluger 1985). This technique has its origin in molecular orbital (MO) theory and has been found to be very reliable in the treatment of the electronic and spatial structure of perfect and defective crystals. Some examples include investigation of hole polarons (Jacobs and Kotomin 1992, Jacobs *et al.* 1993) and F-type complexes (Stashans *et al.* 1994, Kotomin *et al.* 1995) in the corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) crystal, impurity intercalation studies in the TiO<sub>2</sub> crystal (Stashans *et al.* 1996a, b, Lunell *et al.* 1997), H-atom studies in zincblende structure semiconductors (Stashans and Kitamura 1996, 1997) and the equilibrium position detection for H impurities in the WO<sub>3</sub> crystal (Stashans and Lunell 1996).

## §2. BRIEF OUTLINE OF THE METHOD

The method is based on the MO theory and a periodic large-unit-cell (LUC) model. This approach considers the electronic band structure and calculates the total energy of the system very accurately owing to not only the periodicity condition but also a careful treatment of the exchange interaction. This is very important since titanate crystals have considerable covalency effects in the chemical bonding, which have to be taken into account to obtain a reliable outcome. A full account of the method used to calculate the total energy of the crystal within the LUC framework has been given by Stefanovich *et al.* (1990). The main idea of the LUC approximation is that the Fock matrix elements are made self-consistent through terms of the form

$$\frac{1}{N} \sum_{\mathbf{k}} P_{pq}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R}_v), \quad (1)$$

where the summation is carried out over the values  $\mathbf{k}$  in the reduced Brillouin zone (BZ) of the LUC. It has been proved (Shluger and Stefanovich 1990) that the computation of the electronic structure of the unit cell at  $\mathbf{k} = \mathbf{0}$  in the reduced BZ is equivalent to a band-structure calculation at those BZ  $\mathbf{k}$  points which transform to the reduced BZ centre on extending the primitive unit cell. As indicated by numerous studies (Kantorovich *et al.* 1994, Stashans and Kitamura 1997, Zhukovskii *et al.* 1997, Persson *et al.* 1998), a fourfold- or eightfold-symmetric extension of the primitive unit cell proves to be completely sufficient to reproduce correctly the electronic band structure of the crystal. We have used an eightfold ( $2 \times 2 \times 2$ ) extended LUC to study the H impurity in the BaTiO<sub>3</sub> crystal.

The numerical parameters for the BaTiO<sub>3</sub> crystal have been obtained before reproducing the most important properties of this material and also in studies of

Table 1. Semiempirical parameter sets used in the present work:  $\zeta$ ,  $E_{\text{neg}}$ ,  $P^0$  and  $\beta$ .

Atom	AO	$\zeta$ (au)	$E_{\text{neg}}$ (eV)	$P^0$ (electrons)	$\beta$ (eV)
Ba	6s	1.65	6.2	0.2	-0.4
	5p	2.8	34.6	2.0	-4.0
Ti	4s	1.4	3.7	0.65	-0.5
	4p	1.1	-15.0	0.04	-0.5
	3d	1.93	7.2	0.55	-9.0
O	2s	2.27	4.5	1.974	-16.0
	2p	1.86	-12.6	1.96	-16.0
H	1s	1.2	4.0	0.8	-2.0

Table 2. Two-centre parameters  $\alpha_{\mu\text{B}}$  where  $\mu \in \text{A}$ .

A	$\alpha_{\mu\text{B}}$ (au <sup>-1</sup> )			
	B=Ba	B=Ti	B=O	B=H
Ba	0.20	0.10	0.57	0.00
Ti	0.53	0.13	0.38	0.00
O	0.36	0.10	0.15	0.23
H	0.00	0.00	0.42	0.33

other crystals. In particular, parameters for the O 2s and 2p atomic orbitals (AOs) and the H 1s AO are taken from the work of Stefanovich *et al.* (1990), for the Ti 4s, 4p and 3d AOs as well as for the Ba 6s and 5p AOs from the work of Pinto and Stashans (2000). As one can see, we have restricted ourselves to the use of the valence basis set. The parameters utilised are given in tables 1 and 2.

It is important to note that the current computational method has already been applied to titanates, giving encouraging results. In particular, we have studied Nb doping in the cubic and orthorhombic phases of the CaTiO<sub>3</sub> crystal (Erazo and Stashans 2000), hole polarons and impurity centres in the BaTiO<sub>3</sub> crystal (Pinto and Stashans 2000, Pinto *et al.* 2000, Stashans and Pinto 2000, Patiño *et al.* 2001) as well as point-defect studies in the SrTiO<sub>3</sub> crystal bulk and surface (Sánchez and Stashans 2001, Stashans 2001, Stashans *et al.* 2001).

### §3. RESULTS AND DISCUSSION

As was mentioned above, an eightfold- or even fourfold-symmetric extension of the primitive unit cell proves to be sufficient to reproduce correctly the geometry and electronic density distribution of a given crystal. Hence we have chosen to exploit the 40-atom LUC, which corresponds to the eightfold ( $2 \times 2 \times 2$ ) extension of the primitive five-atom unit cell. Additionally, one H atom was inserted in the middle of the LUC, thus giving us the system consisting of 41 atoms. The LUC size was considered to be sufficient to avoid any mutual defect-defect interaction since the H-atom influence does not extend much in the lattice (Stashans and Kitamura 1996, 1997).

Therefore, our model could be called the study of a *single point defect* within the periodic model.

### 3.1. Characteristics of the O—H bonding

In order to find the minimum-energy configuration we have investigated a number of possible sites for the H intercalation. Different types of H geometry optimization have been performed including automated geometry optimization using the downhill simplex method in multidimensions (Press *et al.* 1986). As a result the obtained H equilibrium position is shown in figure 1.

The impurity atom is located almost within the horizontal  $x$ - $y$  plane formed by the O atoms. The calculated distances of the O—H bond length are found to be equal to 0.89 and 0.91 Å in the cubic and tetragonal phases respectively. The O—H bond axis is found to be almost parallel to the  $x$  axis. The computed bond lengths are shorter than the value of 0.97 Å in a free OH<sup>-</sup> group (Huber and Herzberg 1979). Here one has to consider the OH<sup>-</sup> group instead of a neutral OH molecule since the electronic density analysis gives us  $-0.82e$  and  $-0.75e$  for this complex in the cubic and tetragonal structures, respectively. We explain the shorter bond length for the OH<sup>-</sup> complex as due to the rather compact crystalline packing in the BaTiO<sub>3</sub> crystal. It is worth mentioning that recently performed first-principle pseudopotential

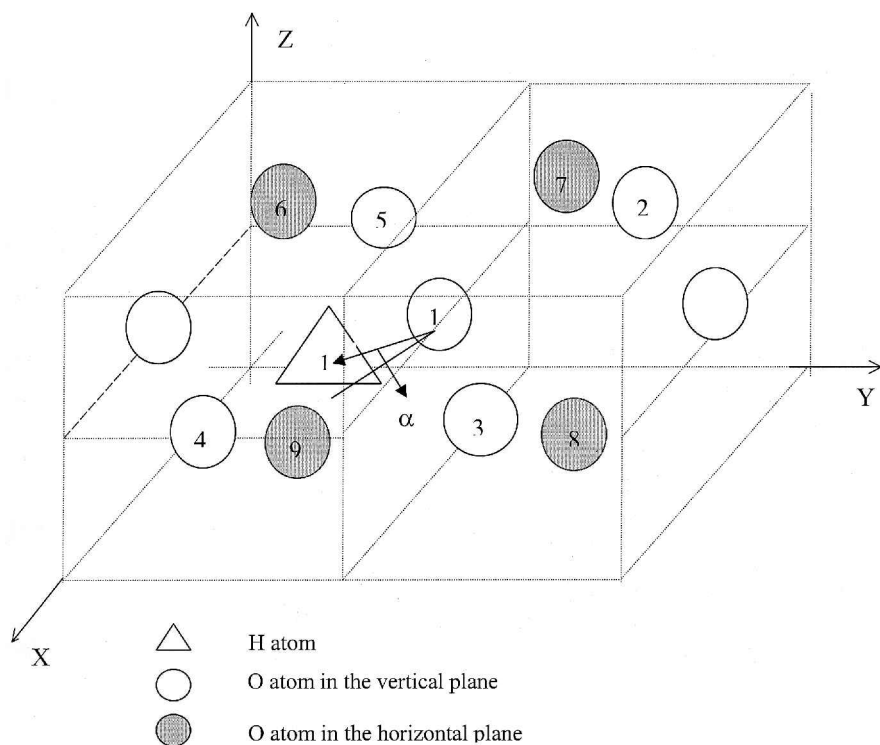


Figure 1. A schematic diagram describing the H equilibrium position in the BaTiO<sub>3</sub> crystal. White and grey circles indicate O atoms located in the middle of vertical and horizontal planes respectively. The impurity atom is located just above the plane formed by O(2), O(3), O(4) and O(5) atoms and forms an angle  $\alpha$  with this plane.  $\alpha = 4.00^\circ$  and  $\alpha = 8.76^\circ$  for the cubic and tetragonal lattices respectively.

calculations based on the local-density approximation of the H atom in the PbTiO<sub>3</sub> crystal (Park and Chadi 2000) also showed a considerable reduction in the O—H bond length in the PbTiO<sub>3</sub> crystal. Obviously the shortening of the O—H bond is a common feature in the titanates because of their compact crystalline lattice.

### 3.2. Lattice response to the H incorporation

The presence of an impurity perturbs the crystalline lattice and, as a result, the atoms closest to the defect move to their new equilibrium sites. The atomic displacements in the cubic structure of the BaTiO<sub>3</sub> crystal show the following pattern. The two Ti atoms closest to the O—H group move outwards by approximately 0.1 Å. The four Ba atoms exhibit the same pattern in their displacements. The two Ba atoms closest to the H impurity move away about 0.17 Å while the two next-closest Ba atoms are displaced by 0.04 Å. The movements of positively charged atoms surrounding the defect are clearly understood if one considers the following two physical effects. Firstly, the H atom is charged positively and thus, owing to the Coulomb interaction, the Ba and Ti atoms move outwards. Secondly, insertion of the H impurity is accompanied by the creation of the chemical bond between this H atom and one of the O atoms, O(1). As a result the chemical bonds between the O(1) atom and the surrounding Ti and Ba atoms are weakened, leading to the outward displacements of these atoms. The Ba and Ti atoms form two atomic spheres surrounding the defect most closely. Since both spheres move outwards, it also provokes the outward movement of some atoms situated in the third sphere surrounding the defect, which consists of the O atoms. Thus we can explain the outward movements of O(4) and O(5) atoms, which receive an imaginary ‘push’ from the atoms of the first two spheres closest to the defect. Complete information on lattice relaxation in the cubic phase of the crystal is given in table 3 and figure 2. Finally, we would like to note that the atomic displacements are not radial with respect to the geometric centre of the system, that is the O—H group. This is expected because the H insertion lowers considerably the local symmetry in the defective region of the BaTiO<sub>3</sub> lattice.

As one can observe, the lattice relaxation in the tetragonal structure of the BaTiO<sub>3</sub> crystal shows a similar pattern (table 4 and figure 3). Because of the lower initial symmetry of the crystal, that is the tetragonal crystallographic structure, the atomic movements are even less ordered. We would like to point out the rather large

Table 3. Outward displacements  $d$  of atoms in the defective region of the cubic BaTiO<sub>3</sub> crystal. Atomic numeration corresponds to that given in figure 2.

Atom	$d$ (Å)
Ba(1)	0.16
Ba(2)	0.18
Ba(3)	0.04
Ba(4)	0.04
Ti(1)	0.10
Ti(2)	0.09
O(4)	0.12
O(5)	0.12

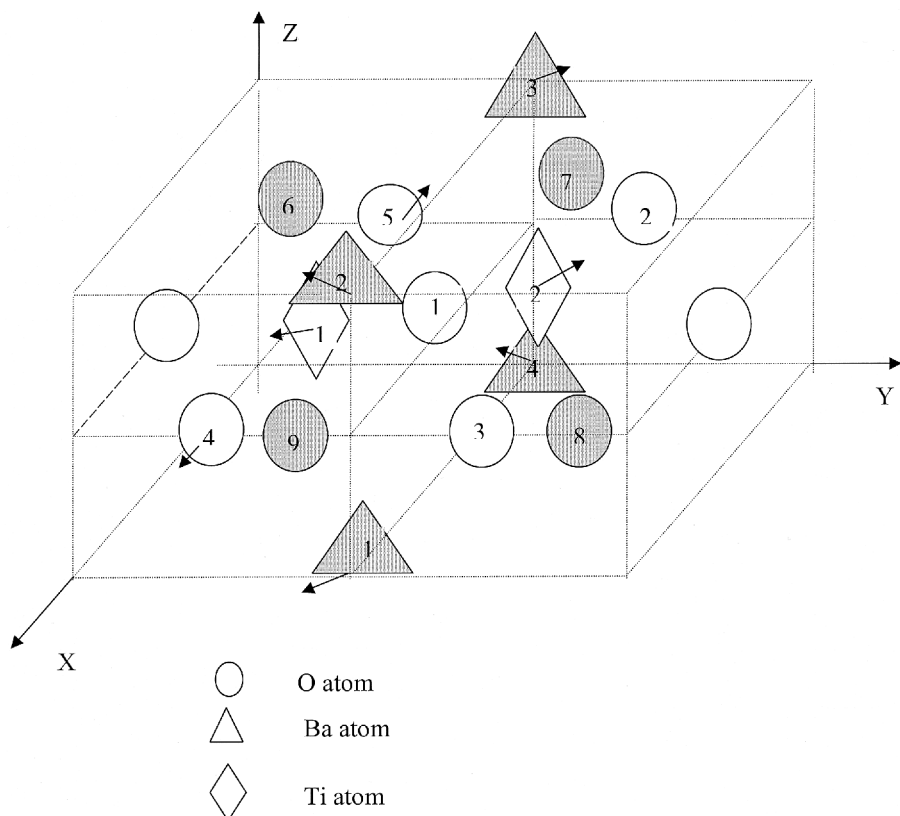


Figure 2. Lattice relaxation in the cubic phase. The arrows show outward displacements of the atoms (with respect to the defect) in the defective region. The H atom is not shown in the figure for simplicity but it forms a chemical bond with the O(1) atom and thus is situated along the positive  $x$  direction.

Table 4. Outward displacements  $d$  of atoms in the defective region of the tetragonal  $\text{BaTiO}_3$  crystal. Atomic numeration corresponds to that given in figure 3.

Atom	$d$ (Å)
Ba(1)	0.08
Ba(2)	0.29
Ba(3)	0.09
Ba(4)	0.08
Ti(1)	0.12
Ti(2)	0.08
O(4)	0.12
O(8)	0.09
O(9)	0.09

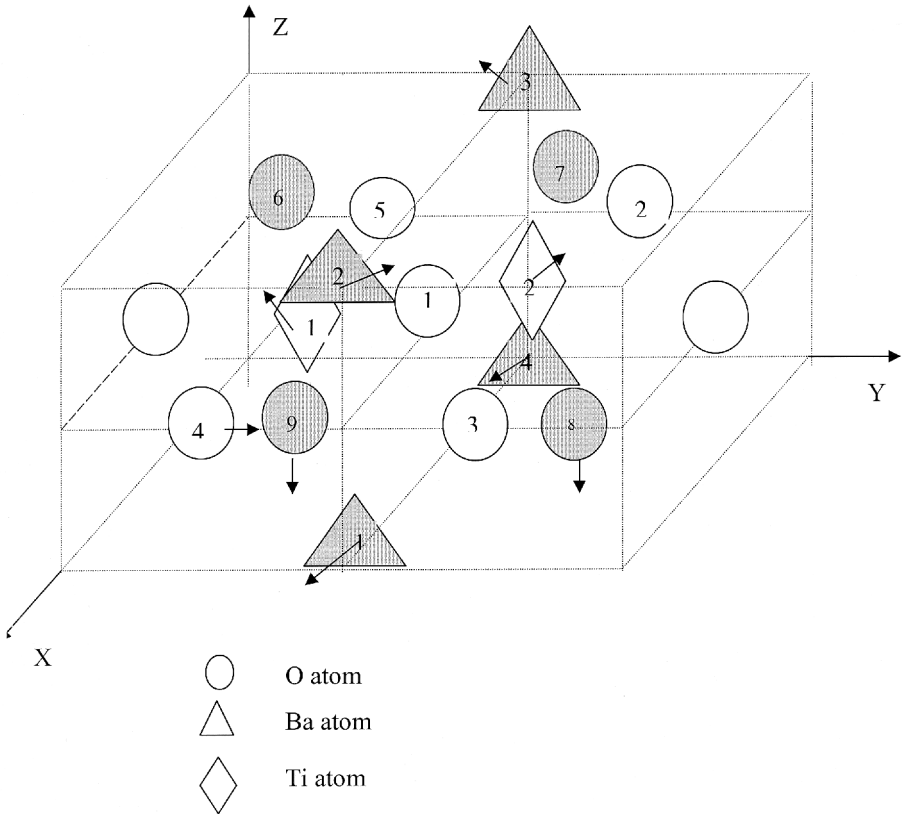


Figure 3. Lattice relaxation in the tetragonal phase. The arrows show outward displacements of the atoms (with respect to the defect) in the defective region. The H atom is not shown in the figure for simplicity but it forms a chemical bond with the O(1) atom and thus is situated along the positive  $x$  direction. The component in atomic displacements along the vertical  $z$  axis is considerably larger than the same variable in the cubic phase.

component of the displacements along the  $z$  axis, especially for Ti(1) and Ba(2). This is normal since in the tetragonal phase the crystalline lattice is slightly extended along the  $z$  axis; so the atoms have more freedom to displace along this direction.

### 3.3. Analysis of the electronic properties in the H-doped BaTiO<sub>3</sub>

The H impurity in BaTiO<sub>3</sub> is found to be an autoionized, positively charged ion since its donor level lies above the conduction-band bottom. In this positively charged state, the valence bands are fully occupied and there is no state in the bandgap. The interstitial H behaves, therefore, as a shallow donor.

The electron density analysis using the Löwdin method, carried out for the equilibrium structures as well as for the doped crystal without lattice relaxation, gives the following pattern. The Ba atoms closest to the impurity almost do not change their effective charges except for the Ba(1) and Ba(2) atoms in the cubic structure (tables 5 and 6). However, we observe considerable charge redistribution for the Ti and O atoms nearest to H. From our results the Ti atoms tend to become less positive while the O atoms become less negative. This implies the redistribution

Table 5. Charges on atoms in the defective region of the cubic BaTiO<sub>3</sub> crystal: perfect crystal,  $Q_1$ ; doped crystal without lattice relaxation,  $Q_2$ ; equilibrium configuration of the doped crystal,  $Q_3$ . Atomic numeration corresponds to that given in figure 2.

Atom	$Q_1$ (units of $e$ )	$Q_2$ (units of $e$ )	$Q_3$ (units of $e$ )
Ba(1)	1.88	1.87	1.81
Ba(2)	1.88	1.87	1.81
Ba(3)	1.88	1.88	1.88
Ba(4)	1.88	1.88	1.88
Ti(1)	2.25	1.90	2.16
Ti(2)	2.25	1.91	1.70
O(1)	-1.38	-1.35	-1.25
O(4)	-1.38	-1.41	-1.25
O(5)	-1.38	-1.36	-1.37
H(1)	—	0.53	0.50

Table 6. Charges on atoms in the defective region of the tetragonal BaTiO<sub>3</sub> crystal: perfect crystal,  $Q_1$ ; doped crystal without lattice relaxation,  $Q_2$ ; equilibrium configuration of the doped crystal,  $Q_3$ . Atomic numeration corresponds to that given in figure 3.

Atom	$Q_1$ (units of $e$ )	$Q_2$ (units of $e$ )	$Q_3$ (units of $e$ )
Ba(1)	1.88	1.87	1.87
Ba(2)	1.88	1.87	1.86
Ba(3)	1.88	1.88	1.88
Ba(4)	1.88	1.88	1.88
Ti(1)	2.02	1.84	1.85
Ti(2)	2.02	1.52	1.54
O(1)	-1.30	-1.30	-1.22
O(4)	-1.30	-1.33	-1.30
O(8)	-1.31	-0.85	-0.83
O(9)	-1.31	-1.27	-1.29
H(1)	—	0.55	0.47

of the electron density from the ions to the chemical bonds, leading to a more covalent character of the chemical bonding in the vicinity of the H impurity. This effect is especially obvious in the tetragonal phase of the crystal (table 6). This also coincides very well with the increase in some interatomic bond lengths in the defective region, leading to the outward atomic movements discussed in the previous section.

An analysis of the spin density reveals that a charge transfer has occurred from the inserted H impurity to the Ti and O atoms nearest to the defect. It is observed that the unpaired electron is occupying Ti 3d<sub>z<sup>2</sup></sub> and O 2p<sub>y</sub> orbitals in the cubic structure and Ti 3d<sub>xz</sub> and O 2p<sub>x</sub> orbitals in the tetragonal lattice. Thus one can see the hybridization between the Ti 3d and O 2p orbitals, producing a more covalent nature in the chemical bonding around the H impurity. It is important to note



the importance of precisely performed lattice relaxation. From tables 5 and 6, it can be seen that the effective charges on atoms are quite different for the final configuration compared with the configuration not considering the lattice relaxation.

### 3.4. H effect on ferroelectric polarization

An important issue concerning impurities and defects in ferroelectric crystals is their effect on the ferroelectric polarization. The BaTiO<sub>3</sub> crystal exhibits ferroelectricity in its tetragonal phase and that is why we investigated possible bulk ferroelectricity changes due to the H insertion. Our qualitative study shows that the absolute values of the effective charges are reduced while the Ti—O bond lengths increase considerably in the defective region. The first effect tries to reduce the electric dipole momentum while the second effect increases it. A simple calculation shows that the second effect, that is the increase in the Ti—O bond lengths is 1.27 times stronger. This indicates that the direction of the new dipole is favourably aligned with the host polarization. Thus, as a result, one can see an increase in the ferroelectric polarization in the BaTiO<sub>3</sub> crystal due to the H impurity. The well-known loss of ferroelectricity by H contamination thus is not a bulk effect. The primary damage is localized at the electrode–ferroelectric interface.

## §4. CONCLUSIONS

The present periodic quantum-chemical calculations evaluate the structural and electronic properties of the BaTiO<sub>3</sub> crystal due to the H impurity. The equilibrium spatial configurations obtained indicate the O—H formation in the crystal. The O—H bond lengths are found to be equal to 0.89 and 0.91 Å in the cubic and tetragonal phases, respectively. Host Ti—O bonds are found to be significantly weakened around a H impurity. This may provide an explanation for O loss in ferroelectric films near the surface under thermal annealing in a H<sub>2</sub> atmosphere (Ikarashi 1998). O loss is enhanced around defective regions and especially at an interface where the hydroxyl ion can react chemically with the electrode (Han and Ma 1997). Damage at the metal–ferroelectric interface can prevent polarization switching and lead to a reduction in the switching charge of the ferroelectric capacitor. As a result of our study we can conclude that the degradation is not a bulk effect since the H impurity increases the bulk ferroelectric polarization.

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