Effect of Interstitial Hydrogen Impurities on Ferroelectric Polarization in $PbTiO_3$

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(Received 27 September 1999)

We investigate the electronic and atomic structure of interstitial hydrogen impurities in $PbTiO_3$ and investigate their effect on ferroelectric polarization through first-principles total-energy calculations. Interstitial H in $PbTiO_3$ is found to bond to oxygen and to act as a shallow donor impurity. At equilibrium, H does not much affect nearby Ti-O bonds and the H-O dipole increases the polarization. The barrier for reversing the defect dipole can give rise to imprint (extra stabilization of one of the two polarization modes).

PACS numbers: 77.80.Dj, 61.72.Ji, 77.84.Dy, 77.80.Fm

An important issue concerning impurities and defects in ferroelectric (FE) crystals is their effect on the ferroelectric polarization. Normally, defects affect ferroelectric devices adversely by giving rise to fatigue (loss of polarization) and imprint (extra stabilization of one of the two polarization modes). Hydrogen is a ubiquitous impurity and its role in such degradation phenomena is currently under intensive investigation [1–9]. When ferroelectrics are used in conjunction with Si, hydrogen contamination during Si passivation can result in a loss of ferroelectricity. Intentional introduction of hydrogen in FE materials has been observed to result in the disappearance of polarization hysteresis, a reduction of the switching charge in FE capacitors, and a decrease of electrical resistance.

Various mechanisms for H-induced degradation have been investigated; however, it is not yet clearly understood whether degradation is a *bulk* effect or whether the primary damage is localized at the electrode-ferroelectric *interface.* Results from a number of experiments indicate that H-induced chemical changes at metal/oxide interfaces are a main source of degradation [1–6]. Degradation is most significant for Pt electrodes and least for conducting oxide electrodes [1,2,5,7]. It has also been suggested that hydrogen can induce the loss of *bulk* ferroelectricity in perovskite ferroelectrics where oxygen loss at the interface, as evidenced by the small change in the lattice parameter after H annealing, is not significant [9]. Hydrogen-induced degradation is often removed and original properties are restored after annealing in O_2 [1,5].

The main purpose of this Letter is to address the question of the effects of interstitial H on the *bulk* properties of a ferroelectric. We chose $PbTiO_3$ as a prototypical perovskite ferroelectric because its phase diagram is simple. It has a tetragonal FE phase ground state which transforms to a cubic phase above 763 K. The ferroelectric phase in this material results from a dimerization between Ti and O atoms along the polarization axis with strong covalent Ti-O bonds alternating with weaker stretched Ti-O bonds [10,11]. The dimerization breaks the inversion symmetry of the cubic lattice and results in a spontaneous polarization.

Defects or impurities can strongly affect the atomic positions in their vicinity and can reduce or enhance the polarization. To examine changes in the polarization induced by a defect we rely on changes in ionic displacements and bonding around the defect [11,12]. An important question concerning H contamination is the effect of its bonding to oxygen on nearby Ti-O bonds, especially those along the polarization axis. Experimental data indicate that hydrogen is interstitially coupled to oxygen [13–18] and that the formation of hydroxyl $[HO]^-$ ions affects Ti-O chains in $Pb(Zr,Ti)O_3$ [6,9].

In this paper we investigate the structural and electronic properties of interstitial hydrogen in bulk $PbTiO_3$ through first-principles calculations. Such calculations have been successfully applied recently to the study of FE perovskites [10,19–21], the energetics of FE domain walls [22], and defects [11,12]. We employ a first-principles pseudopotential method [23] based on the local density approximation [24] with norm-conserving nonlocal pseudopotentials, using the approach of Troullier and Martins [25] and the Kleinman-Bylander type of fully separable pseudopotentials were constructed [26]. The Ceperly-Alder correlation as parametrized by Perdew and Zunger is used [27]. The computational details have been described elsewhere [11]. For simulating the effects of H, we used a $(2 \times 2 \times 2)$ supercell with 40 atoms per cell and a $(2 \times 2 \times 2)$ grid of points for the Brillouin zone summations [28]. The calculated lattice constant for the cubic structure is 3.97 Å, which is in good agreement with the experimental value of 4.04 Å [29].

We first discuss the stable equilibrium site for an interstitial hydrogen impurity in the *cubic nonferroelectric phase* of $PbTiO_3$. We examined the stability of the *A* and *B* sites in Fig. 1 where in each case H is placed between two oxygen atoms. These sites have been previously

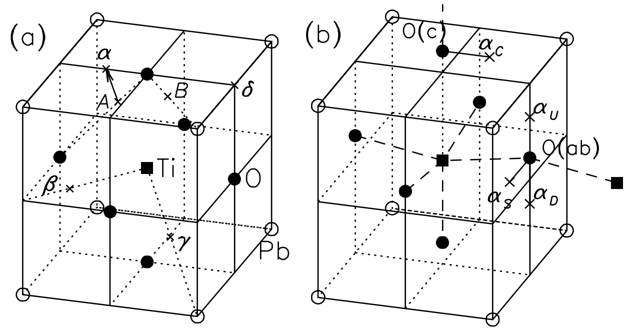

FIG. 1. (a) For the cubic phase of $PbTiO_3$, several of the high symmetry positions tested for interstitial hydrogen are shown by *crosses*. Solid boxes and circles denote Ti and oxygen atoms, respectively; open circles represent Pb atoms. The α site is the most stable one for H. (b) The tetragonal phase contains four distinct α sites: (i) H-O(c) bonding at α_C; (ii) H-O(ab) bonding at α_D, α_S, and α_U sites. The solid and dashed lines describe strong and weak Ti-O bonds, respectively.

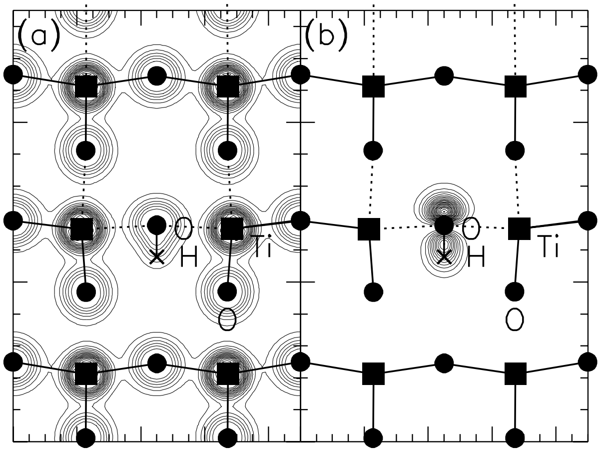

FIG. 2. (a) The relaxed atomic positions around an α-site H and the contours of the total electron density are shown. The contour spacing is 300 electrons/40 atom cell. (b) Contours of electron density of the H-O bonding state with a contour spacing of four electrons/cell.

suggested to be stable positions for H [14–18]. We find them, however, to be unstable with respect to the more stable α site shown in Fig. 1. After examining a number of other configurations, the α site is found to be the most stable one. For other high symmetry sites such as β, γ, and δ, the total energies relative to the α site are, respectively, 0.8 eV, 2.0 eV, and 3.1 eV. A hydrogen atom at α forms a strong bond to a single oxygen atom and the O-H axis is along a cubic axis. The H-O bond length is calculated to be 0.92 Å, as compared to 0.97 Å in a free HO molecule. Using the frozen phonon method, we find the H-O vibration frequency to be 3589 cm^{-1}, close to measured values of around 3460–3700 cm^{-1} in other perovskites [9,14–18].

In order to investigate the interaction of H with the host ionic polarization we tested the relaxation of atoms around an α-site hydrogen in *cubic* $PbTiO_3$. In the presence of hydrogen, a coherent pattern of strong and weak Ti-O bonds along a c axis defined by the O-H bond axis emerges. The relaxed atomic positions of Ti and O atoms together with the contours of the total electron charge density are shown in Fig. 2a. The inversion symmetry of the cubic phase is broken around the H-O defect. The lattice distortions of host atoms are very similar to those of the *ferroelectric* tetragonal phase with the H-O dipole adding to the bulk polarization. The calculated short and long Ti-O bond lengths nearest to the H atom are 1.73 and 2.22 Å and those of the next Ti-O bonds are 1.71 and 2.46 Å, close to the 1.71 and 2.34 Å values in the tetragonal ferroelectric phase. The H-O defect in $PbTiO_3$, therefore, affects the bulk polarizability arising from Ti-O dimerizations only slightly and adds its own dipole to it.

Electrically, hydrogen in $PbTiO_3$ is found to be an autoionized positively charged impurity since its donor level lies above the conduction band minimum. In this positively charged state, the valence bands are fully occupied and there is no state in the gap. Interstitial H behaves, therefore, as a shallow (i.e., effective-mass) donor. Hydrogen doping should enhance the formation of acceptor defects in wide-band-gap crystals [12], since their formation energy is reduced by nearly the size of the band gap for single acceptors and by an even larger energy for multiple acceptors such as Pb vacancies. This provides a possible explanation for the observation that thermal annealing under a hydrogen ambient substantially enhances the loss of Pb [6]. Positively charged hydrogen with no electron of its own can bond to oxygen only through the "lone-pair" p_x or p_y orbitals of oxygen. This is clear from the electron density contours of the H-O bonding state shown in Fig. 2b. The energy level of the H-O bonding state lies about 8 eV below the valence band maximum.

We now examine the energetics of α-site H impurity on the *tetragonal FE phase* of $PbTiO_3$. Oxygen-bonded hydrogen remains a shallow donor impurity in the FE phase. In the tetragonal phase, two kinds of oxygens can be distinguished, as shown in Fig. 1b: (i) O(c) atoms in the dimerized Ti-O-Ti chains along the polarization c axis and (ii) O(ab) atoms in nondimerized Ti-O-Ti chains along the a or b axes. Therefore we can have four kinds of α-site hydrogen impurities: an H-O(c)-type bonding at α_C and three kinds of H-O(ab) bonding sites, α_D, α_S, and α_U, as shown in Fig. 1b. Here it is important to find whether the stable O-H axis is in the same direction as the tetragonal FE polarization or not. If the most stable state for the O-H axis were to lie on an ab plane (at the α_C or α_S sites in Fig. 1b) or at an α_U site [16], then the bulk polarization would be reduced by hydrogen contamination.

The total energies for the various α sites were determined in several steps. First, we examined the energetics in the tetragonally strained lattice with no Ti-O dimerization and no atomic relaxations of the host lattice in order to isolate the strain effect on the energetics. One of the primary cubic axes was elongated in order to examine the effect of tetragonal strain. Tetragonal strain stabilizes the α_C

site H-O(c), which is more stable by 0.19 eV and 0.09 eV than the α_S and α_D (equivalent to α_U) sites of H-O(ab), respectively. The repulsive interactions between a positive H ion and the positive Ti ions make the H bonding to the longer c-axis Ti-O chain favorable. However, the tetragonal strain effect is dominated by the Ti-O dimerization effect. In the ferroelectric lattice with Ti-O dimerizations but with no relaxation of the host lattice, the α_D H-O(ab) site (where the O-H axis is in the same direction as the host lattice polarization) is found to be the most stable. The energies of α_C, α_U, and α_S sites relative to α_D are 0.31 eV, 0.54 eV, and 0.08 eV, respectively. These results indicate that *hydrogen prefers to bond to an oxygen atom along an undimerized Ti-O(ab) chain and that the direction of the H-O dipole is favorably aligned with the host polarization.* When we relax the position of just a hydroxyl $[\mathrm{HO}]^-$ ion, we find that the Ti-O dimerization around the α_C-[HO] ion is locally destroyed as the [HO] ion moves into the center of two nearby Ti atoms and the energy difference between the α_C and α_D sites is slightly reduced to 0.11 eV. Finally when we relax the positions of all atoms fully, the energy difference between the α_C site and the α_D site increases by 1.07 eV.

The reason for the large stability of α_D compared to α_C is that in α_C the Ti-O dimerization is destroyed, whereas in α_D this dimerization makes a significant contribution to the lowering of the total energy. The energy reduction resulting from Ti-O dimerization in FE $PbTiO_3$ is estimated to be about 1.8 eV per 40 atom cell [11], when compared to the reference ideal cubic lattice, and is far more important than the strain effect of 0.19 eV described above in (i).

These results provide an explanation for recent experimental data. Tamura *et al.* [8] found that the change of hysteresis loops depends on the polarization state during the annealing of ferroelectric capacitors in a hydrogen atmosphere. The loops shifted along the voltage axis without a significant change of shape. In the polarized lattice, the concentration of α_D site hydrogen should be high, and this contributes to the shift of the loops. To reverse an H-O dipole, a hydrogen atom needs to move along a relatively long arclength of about 2.9 Å (0.92π), and we estimate the energy barrier of about 0.2 eV for the reversal. A slower response of H to field reversal than that of the bulk polarization can lead to *imprint.*

The results discussed above indicate that hydrogen in bulk $PbTiO_3$ does not necessarily reduce the ferroelectric polarization. However, it is still possible that hydrogen contamination can lead to a reduction in the remnant polarization. We note that our present calculations simulate the ground state at 0 K rather than the state at room temperature and that this can affect the energetics. At high temperatures, the importance of the Ti-O dimerization energy which contributes to the stability of the α_D site is reduced. The tetragonal strain effect reduces the energy difference between sites, resulting in a random mixing of the available α sites. A random distribution of H between the sites would lead to a polarization decrease. A random distribution can occur during annealing above the Curie temperature, where the tetragonal phase transforms to a cubic one, and all α sites become equivalent. It can also occur during fast repeated switchings of the polarization where the switching of the H-O dipolar axis takes place over a longer time scale.

Host Ti-O bonds are found to be significantly weakened around a hydrogen impurity with two Ti atoms being pushed away from the hydroxyl ion. This is evident from the total electron density around the hydrogen shown in Fig. 2a. To examine in more detail the coupling between the hydroxyl ion with Ti atoms, we calculated the variation of the atomic forces on Ti atoms as the hydroxyl ion is displaced and compared it to the case where a single oxygen atom, in the absence of H, is displaced in pure $PbTiO_3$, as shown in Fig. 3. The induced forces on nearby Ti atoms in the former case are found to be much smaller than those in the latter case, indicating the weakening of Ti-O bondings around H.

This may provide an explanation for oxygen loss in FE films near the surface under thermal annealing in a hydrogen atmosphere [3,4,6]. Oxygen loss is enhanced around defective regions such as at surfaces, interfaces, and grain boundaries and especially at an interface where the hydroxyl ion can chemically react with the electrode [1–4,6]. As a result, a ferroelectric capacitor can be damaged even at annealing temperatures where oxygen diffusion is not expected to be significant [9]. Damage at the metal/ferroelectric interface can prevent polarization switching and lead to a reduction of the switching charge of the ferroelectric capacitor. The weakening of Ti-O bonds should change the local vibrational mode of Ti-O and the distortion in Ti-O coordination, which have been suggested through Raman data and [9] electron energy-loss spectroscopy data [6]. We have also calculated atomic forces

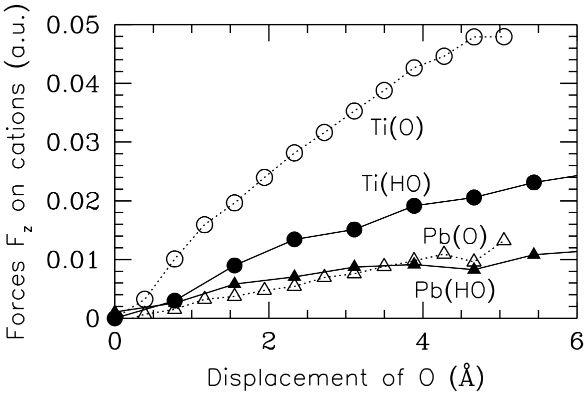

FIG. 3. As an HO ion at an α site moves along the z direction in Fig. 1a, the resultant z components of atomic forces on a Ti atom and a Pb atom nearest to the O atom are described by solid circles and triangles. For comparison, the results for the case of the displacement of a single oxygen atom in cubic $PbTiO_3$ are shown by open circles and triangles.

on the nearby Pb atoms. They were found to be much smaller compared to the forces on Ti which is consistent with a much weaker Pb-O than Ti-O bonding. The forces on Pb atoms are about the same with or without H incorporation. Even though Pb-O bondings are not much affected by H, Pb loss is expected because of the reduction in the formation energy of acceptorlike Pb vacancies noted above and considering the weak Pb-O couplings.

In summary, through first-principles pseudopotential total energy calculations, we find that hydrogen bonds interstitially to oxygen in $PbTiO_3$ and that at equilibrium an H-O defect's polarization is aligned with that of the bulk. The energy barrier for reversing the H-O dipole axis can result in polarization imprint.

C. H. P. acknowledges the support of the Korea Research Foundation (Project No. 1998-001-D00305) and the NEC Research Institute where part of this work was done and thanks M. S. Jang and J. H. Ro for useful discussions.

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