Strain-induced ferroelectric phase transitions in incipient ferroelectric rutile TiO_2*

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Uniaxial strain induced ferroelectric phase transitions in rutile TiO_2 are investigated by first-principles calculations. The calculated results show that the in-plane tensile strain induces rutile TiO_2, paraelectric phase with $P_{4-2/mnm}$ (D_{4h}) space group, to a ferroelectric phase with $P_m(C_s)$ space group, driven by the softening behaviour of the E_u1 mode. In addition, the out-of-plane tensile strain, vertical to the *ab* plane, leads to a ferroelectric phase with P_{42nm} (C_{4v}) space group, driven by the softening behaviour of the A_{2u} mode. The critical tensile strains are 3.7% in-plane and 4.0% out-of-plane, respectively. In addition, the in-plane compression strain, which has the same structure variation as out-of-plane tensile strain due to Poisson effect, leads the paraelectric rutile TiO_2 to a paraelectric phase with P_{nnm} (D_{2h}) space group driven by the softening behaviour of the B_{1g} mode. These results indicate that the sequence ferroelectric (or paraelectric) phase depends on the strain applied. The origin of ferroelectric stabilization in rutile TiO_2 is also discussed briefly in terms of strain induced Born effective charge transfer.

Keywords: TiO_2, epitaxial strain, ferroelectric phase transition, first-principles calculations

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1. Introduction

Incipient ferroelectric, such as $SrTiO_3$, $KTaO_3$, $CaTiO_3$, and rutile TiO_2, is like a ferroelectric material in its paraelectric phase and shows a rapid increase of dielectric constant with temperature decreasing, but it has no ferroelectric phase transition even at absolute 0 K. The quantum fluctuation is suggested to be responsible for the absence of this low-temperature ferroelectric phase.[1−3] In principle, the quantum effect is suppressed by a small perturbation. For instance, small additions of Ca and Ba can induce a ferroelectric phase transition in $SrTiO_3$ with the transition temperature T_c is proportional to $(x - x_c)^{1/2}$, where x is the impurity molar concentration and x_c is the critical concentration.[4,5]

It has been theoretically accepted that the isotropic expansion of volume results in a ferroelectric phase transition in incipient ferroelectrics, such as $KTaO_3$[6] and $CaTiO_3$.[7] In our previous work, we showed that negative hydrostatic pressure can transform incipient paraelectric rutile TiO_2 with a $P_{4-2/mnm}$ (D_{4h}) space group into a true ferroelectric phase with a P_{42nm} space group,[8] which is in good accordance with Montanari's results.[9] Isotropic expansion or negative hydrostatic pressure remains a challenge especially for application in devices. Monanari[9] showed that uniaxial expansion along the *c* axis offers a possibility to induce a ferroelectric phase transition in rutile TiO_2. However, the sequential TiO_2 ferroelectric phase has not been characterized. Meanwhile, the in-plane strain, which has been proved to be highly effective in driving incipient ferroelectric to true ferroelectric in epitaxial film of $SrTiO_3$,[10] has not been studied either.

In the present work, we report on our calculated results of the strain induced ferroelectric phase transition in rutile TiO_2. Both in-plane and the out-of-plane strain are used and the sequential phases are characterized based on phonon mode calculations at Γ point. In particular, we suppose the ferroelectric phase transitions in present simulation are purely displacive, which is reasonable in the case of rutile TiO_2.[8]

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2. Method details

The first-principles density-functional theory (DFT) within the local density approximation (LDA) was employed to perform the theoretical investigation. The extended norm-conserving pseudopotentials, which include more states as semi-core than in the Troullier–Martins', were used for all atoms,[11] with considering Ti(3s, 3p, 3d, 4s) and O(2s, 2p) orbits by using plane waves with a cutoff energy of 55 Hartree. A 6×6×8 Monkhorst–Pack's mesh was chosen to perform the integration in the reciprocal space. All parameters were tested and showed enough convergence for the energy calculations.

To investigate the effects of in-plane or out-of-plane strains, a restricted structural optimization was carried out. For the in-plane strain, the lattice parameters, a and b, were constrained while c and the internal atomic coordinates were fully relaxed symmetrically. For the out-of-plane strain, c was constrained while a, b and the internal atomic coordinates were fully relaxed. The in-plane and the out-of-plane tensile strains are shown schematically in Figs. 1(a) and 1(b), respectively. The convergence of structural optimization required the Hellmann–Feynman force to be less than 10^{-6} Hartree/Bohr ($\approx 5\times10^{-5}$ eV/Å, 1 Å=0.1 nm). The phonon frequencies, the dielectric tensors, and the Born effective charges were calculated based on the density-functional perturbation theory (DFPT).[12] The ground-state results of rutile TiO_2 has been reported, exhibiting good agreement with the experimental values.[8]

All of these simulations were performed by using the ABINIT software package[13] at cluster Lenovo 1800.

3. Results and discussion

Starting from the fully relaxed structure,[8] the in-plane and the out-of-plane tensile strain dependences of phonon frequencies at the Γ point were calculated as shown in Fig. 1(c) and Fig. 1(d), respectively. The curves in Fig. 1(c) indicate that all vibration modes in the unit cell, except the B_{1g} and E_u3, become softer as the in-plane tensile strain increases. The three softest modes, E_u1, A_{2u}, and B_{1u}, gradually develop into negative values at the in-plane tensile critical strains of 3.7%, 4.5%, and 5.9%, respectively. Figure 1(d) shows that all modes, except the B_{1g} and E_u2, become softer as the out-of-plane tensile strain increases. The three softest modes, A_{2u}, B_{1u} and E_u1, turn negative from the out-of-plane tensile strains 4.0%, 5.0%, and 8.0%, respectively. Such results consist with Montanari's results.[9] The tendencies observed from Fig. 1 are different from the relative calculating results under negative hydrostatic pressure, where the three lowest modes are A_{2u}, E_u1 and B_{1u} and only the B_{1g} mode is abnormal.[8] On the basis of the factor group analysis, the sequential phases corresponding to the softening behaviours of E_u1 and A_{2u} modes have P_m and P_{42nm} space groups, respectively. Both phases are possible ferroelectrics due to their polar point groups of C_s and C_{4v}, respectively, and the corresponding spontaneous polarizations lie in and out of the planes for P_m and P_{42nm} space groups, respectively.

To explore the strain-induced ferroelectric phase transition in rutile TiO_2, further calculations have been performed to generate the tensile strain dependence of unit cell volume, spontaneous polarization P_s and dielectric tensor as shown in Fig. 2. Considering that the crystal is purely ionic by neglecting the electronic polarization, the spontaneous polarization, P_s, can be obtained from $P_s = \Sigma Z_i^* v_i / V$, where V is the volume of unit cell, v_i is the displacement of the i-th atom from its corresponding position in the paraelectric phase and Z^* is the Born effective charge. The values of P_s are positive at the phase transition points, 3.7% in-plane tensile strain and 4.0% out-of-plane tensile strain, and reach the maxima of 30 $\mu C/cm^2$ at 5% in-plane tensile strain and 45 $\mu C/cm^2$ at 6% out-of-plane tensile strain, respectively. Therefore the out-of-plane tensile strain is more efficient than the in-plane tensile strain in realizing a large P_s. The reason is that there is only one polar mode out-of-plane, A_{2u}, whereas there are three polar modes in-plane, E_u1, E_u2, and E_u3, therefore the influence of enlarging lattice constant on the E_u1 mode is smaller than that on the A_{2u} mode.[9] The calculated dielectric tensors along the c axis under the out-of-plane tensile strain, d_{33}, and along the a axis under the in-plane tensile strain, d_{11}, show dramatic increases in the vicinity of phase transition, 3.7% and 4.0%, relatively. The peak values are hundreds of times larger than the values in the ground state, implying a ferroelectric phase transition. Both strain dependences of unit cell volume show continuous increase as the tensile strain increases, showing that both the in-plane and the out-of-plane tensile strains induced phase transitions exhibit second-order characters.

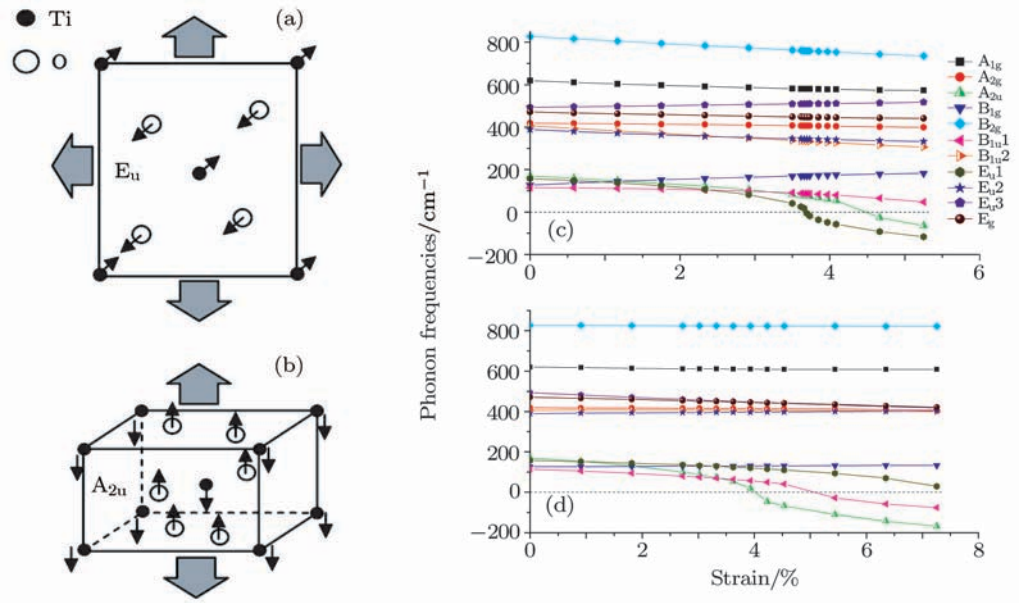


Fig. 1. (colour online) Schematic diagrams of atomic displacements associated with the eigenvector corresponding to the A_{2u} and E_u modes ((a) and (b)) and strain dependence of phonon frequency at Γ point of rutile TiO_2 ((c) and (d)). Panels (a) and (c) correspond to the in-plane tensile strain while panels (b) and (d) correspond to the out-of-plane tensile strains. Grey arrows in panels (a) and (b) show the directions of strains.

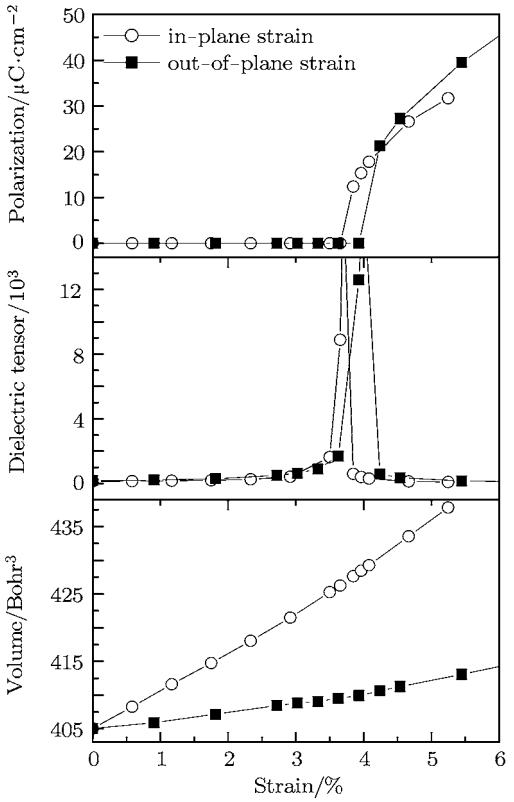


Fig. 2. Polarization, dielectric tensors and volume versus tensile strain.

Since the single-direction lattice extension is admirably used in practical devices, the in-plane compression can generate a lattice expansion out of the plane due to the Poisson effect when materials grow epitaxially on a substrate with small lattice mismatch. Thus the in-plane compression strain may soften the A_{2u} mode and lead to a more efficient ferroelectric phase transition as suggested in Ref. [9]. The further calculated in-plane compression strain dependence of vibration mode, however, presents a different result as shown in Fig. 3.

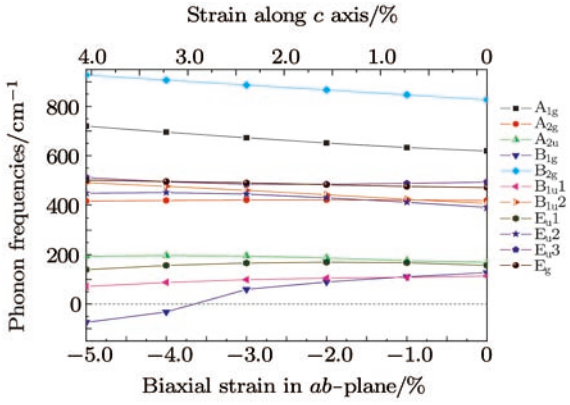


Fig. 3. (colour online) In-plane compression strain dependences of phonon frequency at Γ point of rutile TiO_2.

As expected, the in-plane compression strain generates a lattice out-of-plane expansion. The Poisson ratio, governed by $\upsilon_{ac} = -\varepsilon_c/\varepsilon_a$, can be fitted very well to a linear polynomial as a function of ε_a, $\upsilon_{ac} = (0.6755 - 0.0588) \times \varepsilon_a$, in a range of ε_a from -5.5% to 5.5%. However, the A_{2u} mode becomes stiffer but not softer as lattice constant c increases. The vibration modes, A_{2g}, B_{1u}, E_u1, and E_u3, reach the extremum values in the strain range. The critical

values of in-plane compression strain are −1.5%, 0.0%, −2.0%, and −3.0% for the A_{2g}, B_{1u}, E_u1, and E_u3 modes, respectively. Thus the mode Grüneisen parameter, which describes the pressure dependence of vibration frequency, is not a linear function of strain. The B_{1g} mode, instead of the speculated A_{2u} mode, is the first one to become negative at an in-plane compression strain of −3.6%. The eigendisplacement of the B_{1g} mode changes the paraelectric rutile TiO_2 with $P_{4-2/mnm}$ (D_{4h}) space group into a paraelectric phase with space group P_{nnm} (D_{2h}), indicating that the in-plane compression strain cannot induce a ferroelectric phase transition.

Decreases in a and b lattice constants truely cause an increase in c lattice constant, and *vice versa*. After the restricted structural optimization, the resident stress along the c axis is zero when the in-plane compression strain is applied. On the other hand, when the out-of-plane tensile strain is applied the resident stress along the c axis is proportional to the strain after the restricted structural optimization. Therefore even with a nominally identical strain along the c axis the calculated vibration frequencies are different under the conditions between the in-plane compression strain and the out-of-plane tensile strain. That is the fact that the results reported in Fig. 1(d) are not identical to the results reported in Fig. 3 (the part related to an expansion strain along the c axis up to 4% scaled is on the top of the figure).

To investigate the origin of ferroelectric instability of rutile TiO_2 under strain, the values of Born effective charge tensor, Z^*, were calculated as a function of in-plane tensile strain and out-of-plane tensile strain as shown in Figs. 4(a) and 4(b), respectively. Although it is reported that Z^* is quite insensitive to structural details,[14] figure 4 exhibits the influence of strains on Z^*. The dash line shows the critical strain of phase transition. The calculated Z^* shows the anomalously large values, suggesting that a strong dynamic charge transfer occurs along the Ti–O bond. As the strain increases, the absolute value of Z^* along the expansion direction decreases while that along the compression direction increases instead. For instance, when the in-plane tensile strain increases from 0 to 3.7%, i.e. expanding the a and b lattice constants and compressing the c lattice constant in Fig. 4(a), Z^* of Ti along the a axis, Ti_{11}, decreases from 6.31 to 5.80, Z^* along the c axis, Ti_{33}, increases from 7.57 to 7.77, and O_{11} decreases from −3.16 to −2.91, O_{33} increases from −3.79 to −3.80. This reveals that the Ti–O bonding along the expansion direction becomes more covalent and that along the compression direction becomes more ionic with the increase of strain. The charge transfer from O to Ti ions induced by tensile strain suggests an increase of the hybridization between O_{2p} and Ti_{3d} orbitals, which reduces short-range repulsion and stabilizes the ferroelectric distortion. This effect prevails in most titanate perovskite ferroelectric oxides. The result also explains that the spontaneous polarization lies in the expansion direction because the ferroelectric phase favours lower compression, larger volume, and more covalent bonding system. Experiencing ferroelectric phase transitions, all Born effective charge tensors decrease in all directions with the strain increasing, consisting with the fact that ferroelectric phase favours more covalent bonding.

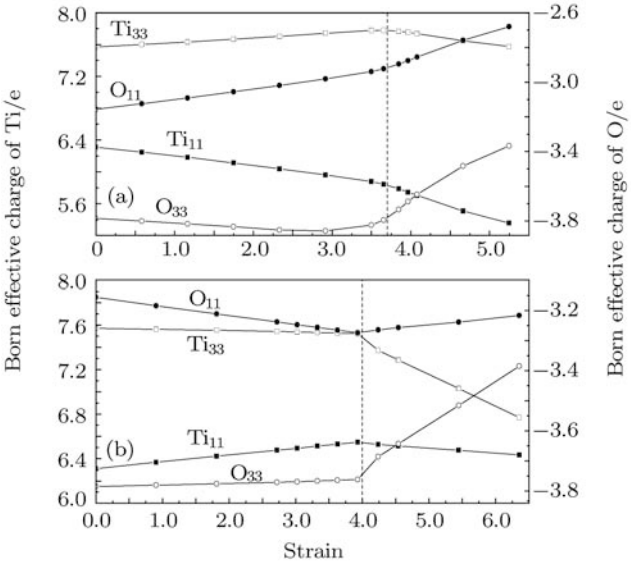


Fig. 4. Strain dependences of Born effective charge tensor of rutile TiO_2: (a) in-plane tensile strain, (b) out-of-plane tensile strain. Subscript 11 and 33 represent Born effective charge tensors along x and z directions, respectively; dashed lines denote the strain where the phase transition occurs.

4. Conclusions

We performed the *ab initio* calculations to investigate the in-plane and the out-of-plane strain induced ferroelectric phase transitions in rutile TiO_2. The in-plane tensile strain and the out-of-plane tensile strain can induce the paraelectric rutile TiO_2 to ferroelectric phases with P_m (C_s) and P_{42nm} (C_{4v}) space groups, respectively, associated with the softening behaviours of E_u1 and A_{2u} vibration modes. Both ferroelectric phase transitions exhibit a second-order character. Due to the Poisson effect the in-plane com-

pression drives an out-of-plane expansion, leading to a paraelectric phase transition associated with the softening behaviour of the B_{1g} mode. The Born effective charge analysis suggests that the ferroelectric instability in rutile TiO_2 originates from a charge transfer from O to Ti to enhance the Ti_{3d}–O_{2p} orbits hybridization, driven by the lattice expansion.

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