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Theoretical study on martensitic-type transformation path from rutile phase to α-PbO_2 phase of TiO_2*

Wen-Xuan Wang(王文轩)[1], Zhen-Yi Jiang(姜振益)[1,†], Yan-Ming Lin(林彦明)[1], Ji-Ming Zheng(郑继明)[1], and Zhi-Yong Zhang(张志勇)[1,2]

[1] *Shaanxi Key Laboratory for Theoretical Physics Frontiers, Institute of Modern Physics, Northwest University, Xi'an* 710069, *China*
[2] *Stanford Research Computing Center, Stanford University, Stanford, California* 94305, *USA*

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The martensitic-type phase transformation paths from the rutile to the α-PbO_2 phase of TiO_2 are studied with linear interpolation and NEB/G-SSNEB methods based on first-principles calculations. Its potential energy surface and the lowest energy path are revealed. Our results indicate that the titanium atoms of the rutile phase shuffle along the $[0-11]_{rut}$ crystal direction to form the α-PbO_2 phase. During the phase transition, the oxygen atoms are dragged by the heavier titanium atoms and then reach their new equilibrium positions. The barrier of phase transition from nudged elastic band theory is about 231 meV, which is qualitatively consistent with previous theoretical calculations from the monoclinic phase to the tetragonal phase for ZrO_2 and HfO_2. Debye model can also be successfully used to predict the pressure and temperature of the phase transformation.

Keywords: phase transition, transition barrier, Debye's theory, NEB method

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1. Introduction

Superhard materials have a combination of high hardness, high melting point, corrosion resistance, and wear resistance, and are widely used in many fields, such as machining, oil and gas exploration, and marine equipment.[1–5] The research on the preparation of superhard materials by the pressurized method is more and more extensive with the maturity of high-pressure technology in recent years.[6] A new orthorhombic structure ($PbCl_2$ with *Pnma* symmetry) of titanium dioxide has been synthesized at pressures above 60 GPa and temperatures above 1000 K, which has potential applications in the field of superhard materials.[7] However, after the pressure drops to environmental pressure, the material will lose its stability and utilization value. The reason for the instability of high pressure phase is that the titanium dioxide will transform into monoclinic baddeleyite, orthorhombic columbite, and rutile phases in the depressurization process.

The tetragonal rutile phase is the most stable structure in ambient conditions for titanium dioxide TiO_2.[8] With the increase of pressure, the rutile phase will irreversibly transform to the orthorhombic α-PbO_2 phase at room temperature,[9,10] and then continue to transform to baddeleyite phase accompanied by $\sim 20\%$ volume reduction.[11,12] After pressure releases, the baddeleyite phase can easily return to the α-PbO_2 phase at room temperature, and then reverts to the rutile phase only when the temperature is above about 450 ℃.[10] The crystallographic relationship and habit plane between this the α-PbO_2 type TiO_2 slab and twinned rutile host can be explained by a martensitic-type transformation.[13] The structural transition from the rutile to the α-PbO_2-type TiO_2 structure can be achieved by shearing on the $\{011\}$ plane of the rutile. However, up to date, there has no theoretical study about understanding the mechanism of martensitic-type transformation between the rutile and the α-PbO_2 phase on an atomic scale. Why is it irreversible for transition from the rutile to the α-PbO_2 phase at room temperature? Our theoretical researches may lay a theoretical foundation for solving the problem of high pressure phase instability.

2. Computational details

Our calculations were performed with the plane-wave basis set with the projector augmented wave (PAW).[14,15] Density functional theory (DFT) calculations within the generalized gradient approximation (GGA)[16] were carried out by using the Vienna *ab initio* simulation package (VASP).[17,18] The Brillouin zone integration was chosen by using the special $5\times5\times5$ k-point sampling of the Monkhorst–Pack type. The kinetic energy cutoff of 500 eV was found to ensure the total energy convergence to 10^{-6} eV/atom. The full structural relaxation was performed until the Hellmann–Feynman forces were less than 0.02 eV/Å. The $[01-1]$ and $[011]$ directions of the rutile phase were chosen as the $[010]$ and $[001]$ directions of the new cell, respectively. The experimentally obtained structural data were used as input to the geometric optimization calculation for new unit cell. The total energy

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†Corresponding author. E-mail: jiangzhenyi@nwu.edu.cn
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calculations along the migration path of the atom and the rotation of the cell were used to plot the possible paths. The NEB and G-SSNEB methods[19–21] were used to estimate the transformation energy barrier. The VASP software was used to optimize the rutile phase and the α-PbO_2 phase under different pressure conditions to obtain a stable structure. The VASPKIT software was used to obtain the Gibbs free energy values at different temperatures and pressures, and the phase transition temperature and pressure were further obtained.

3. Results and discussion

3.1. Phase transition from linear interpolation method

Martensitic-type transformations have certain crystallographic characteristics. The two phases involved in a martensitic-type transformation should have a lattice correspondence and orientation relationship, or a strain invariant plane, and an atom-to-atom correspondence.[22]

The rutile and α-PbO_2 phase of TiO_2 hold D_{4h}^{14} and D_{2h}^{14} space groups, respectively. Each titanium atom is coordinated with six oxygen atoms to form an octahedron in rutile and α-PbO_2 phases[23] as shown in Fig. 1.

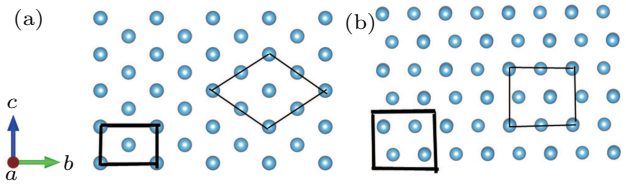


Fig. 1. Crystallographic unit cell (thick line) and new reselection of crystal cell (thin line) for (a) rutile phase and (b) α-PbO_2 crystal phase.

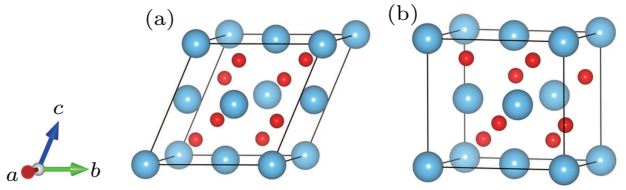


Fig. 2. Crystal cell of rutile and α-PbO_2 phase for (a) rutile phase and (b) α-PbO_2 phase (red: oxygen atoms, blue: titanium atoms).

The octahedron in the α-PbO_2 phase is severely distorted.[24] There exists a group–subgroup relationship between the symmetry groups of the tetragonal parent and orthorhombic product phases due to their identical [100] crystal orientation. Their specific crystallographic correspondences are $[100]_\alpha||[100]_{\rm rut}$ and $(001)_\alpha||(011)_{\rm rut}$.[13] Previous pressure-induced transition experiments[25] also revealed that the applied shears normal to the optic (tetragonal) axis of rutile are most effective for inducing the transition, so we re-establish the new crystal cells of the rutile and α-PbO_2 phase as shown in Fig. 2 to simulate the martensitic-type transition path.

Because the martensitic transformation involves the continuous shear of the crystal cell and the alternate atomic shuffle, the potential energy surface and the minimum energy path each are a function of internal atomic coordinates and lattice constants of the crystal cell. First, the lattice correspondence between the rutile phase and the α-PbO_2 phase is established. The vector set of the rutile phase containing 12 atoms is

$$\eta_{\rm rut} = \begin{pmatrix} 4.6433 & 0.0000 & 0.0000 \\ 0.0000 & 5.5105 & 0.0000 \\ 0.0000 & 2.3138 & 5.0013 \end{pmatrix} \begin{matrix} \cdots\ a_{\rm rut}, \\ \cdots\ b_{\rm rut}, \\ \cdots\ c_{\rm rut}, \end{matrix} \tag{1}$$

where $a_{\rm rut}$, $b_{\rm rut}$, and $c_{\rm rut}$ represent the three axes of the rutile phase, respecticely. The vector set of α-PbO_2 phase containing 12 atoms is

$$\eta_\alpha = \begin{pmatrix} 4.5848 & 0.0000 & 0.0000 \\ 0.0000 & 5.5781 & 0.0000 \\ 0.0000 & 0.0000 & 4.9365 \end{pmatrix} \begin{matrix} \cdots\ a_\alpha, \\ \cdots\ b_\alpha, \\ \cdots\ c_\alpha, \end{matrix} \tag{2}$$

where a_α, b_α, and c_α represent the three axes of α-PbO_2 phase, respectively. The lattice correspondence of the rutile phase to the α-PbO_2 phase is $a_{\rm rut} \to a_\alpha$, $b_{\rm rut} \to b_\alpha$, $c_{\rm rut} \to c_\alpha$. In the process of converting the rutile into the α-PbO_2 phase, the coordination number of the titanium atom is unchanged. Therefore, we assume that an atomic correspondence guarantees the minimum displacement of atoms. The fractional coordinates of the rutile phase and the α-PbO_2 phase are written as $\{V_{\rm rut}^{i,\beta}\}$ and $\{V_\alpha^{i,\beta}\}$, respectively, where i corresponds to the number of atoms and $\beta = x, y, z$. In fact, the potential energy surface is a function of lattice parameters and atomic coordinates. In order to simplify the potential energy surface, we adopt the following approximation. The lattice parameters change uniformly with the phase transition, and the atomic coordinate changes uniformly with phase transition. Now we can write the potential energy surface as a function of two parameters[26]

$$E(x,y) = E(\{\eta_x\},\{V_y\}). \tag{3}$$

Here x and y are determined by linear interpolation, with $\eta_x = (1-x)\eta_{\rm rut} + x\eta_\alpha$ being the lattice vector collection. The $V_y^{i\beta} = (1-y)V_{\rm rut}^{i\beta} + yV_\alpha^{i\beta}$ is a set of fractional atomic coordinates describing the state of the system between two phases, where x and y vary from 0 to 1, with 0 representing the rutile phase and 1 denoting the α-PbO_2 phase. We use x and y as the variable to describe the potential energy surface for the transition from the rutile phase to the α-PbO_2 phase as shown in Fig. 3. The letters A–B–C–D–E–F indicate the minimum energy reaction paths in Fig. 3.

The structural change on the lowest energy path of the phase transition is shown in Figs. 4(a)–4(f), which corresponds to the A–B–C–D–E–F structures in Fig. 3. The energy barrier of the phase transition from the rutile phase to the α-PbO_2 phase is 398 ± 50 meV after zero point correction. Our results are qualitatively consistent with previous theoretical simulations from the monoclinic phase to the tetragonal phase for

ZrO_2 (170 meV/ZrO_2) and HfO_2 (210 meV/HfO_2).[26] It may be easier for the phase transition from the monoclinic to the tetragonal phase to take place, resulting in a lower potential barrier.

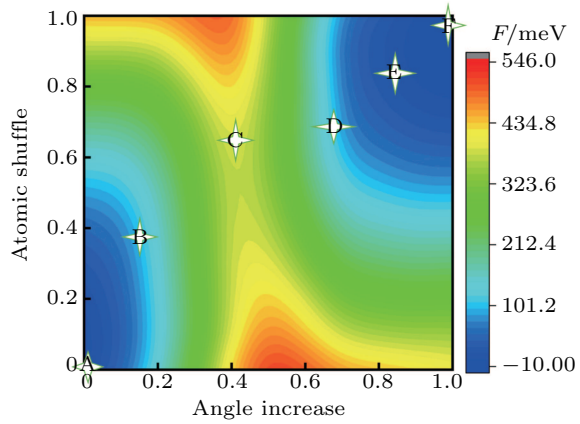


Fig. 3. Potential energy surface during rutile phase transiting to α-PbO_2 phase with A–B–C–D–E–F representing points on minimum energy path.

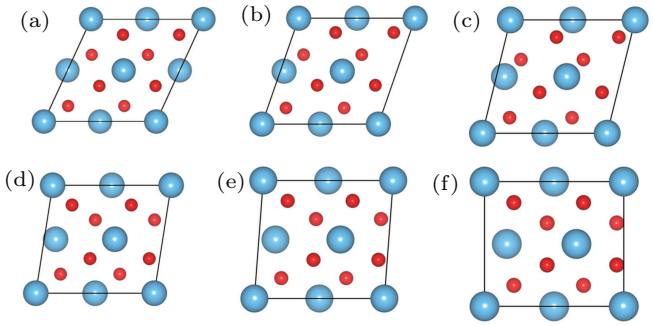


Fig. 4. (a)–(f) Structural alternations during phase transition.

3.2. Phase transition from NEB method

The energy barrier of phase transition from the rutile phase to the α-PbO_2 phase by the NEB[19,20] and G-SSNEB[21] methods are about 231 meV and 234 meV, respectively, as shown in Fig. 5. The positions of titanium atoms at the highest barrier in Fig. 5 are close to those of titanium atoms in Fig. 4(d), and the position difference between oxygen atoms are larger. All titanium atoms shuffle along the $[0-11]_{rut}$ crystal direction during the phase transition, and oxygen atoms are dragged to a new equilibrium position, which is derived from their larger vibration amplitude in our phonon spectra (Due to the limitation to paper length, no more illustrations are given here). All oxygen atoms move along a zigzag path rather than a simple slip path, which can avoid significantly increasing the potential energy, and eventually reach their new equilibrium positions. The straight-line sliding of titanium atoms and the zigzag dragging of oxygen atoms form the complex martensitic transformation, so-called martensitic-type transition. Our NEB barrier is much smaller than that (398 ± 50 meV) from the linear interpolation method. The NEB calculation allows not only all atoms to deviate from the direction $[011]_{rut}$ perpendicular to the atomic slip $[0-11]_{rut}$, but also the cell volume to change in the optimization process. However, the linear interpolation method requires the cell volume and atomic sliding direction to be fixed. Therefore, the potential barrier from the NEB method will be much lower than that from the linear interpolation method. If the number of middle structures with linear interpolation method increases, the same results as those of NEB can be obtained theoretically.

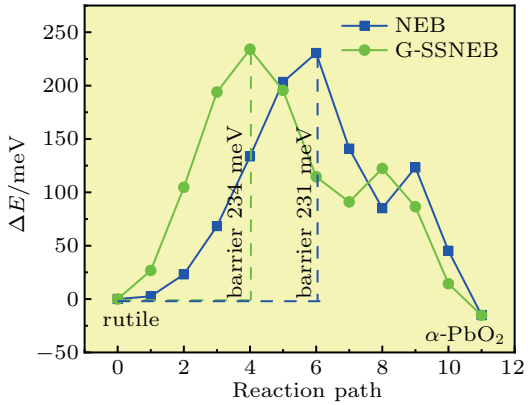


Fig. 5. Phase transition barrier from rutile phase to α-PbO_2 phase of TiO_2.

Under an external high pressure, the martensitic-type transformation is very rapid. In fact, the atoms in the crystal cell are not able to relax to the instantaneous equilibrium positions without enough time in the process of phase transition, so the phase transition barrier obtained by the linear difference method may be closer to the actual barrier. Even so, the NEB barrier is still of great significance in the field of physics, because this value is closer to the lowest barrier in the quasi-static process of solid phase transition.

Jamieson and Olinger reported the transition from the rutile to the α-PbO_2 phase at 10 GPa and 400 ℃.[27] And the α-PbO_2 phase can revert into the rutile phase at temperatures above 450 ℃ after pressure has been released.[10] The average kinetic energy per TiO_2 in the ideal gas model is 203 meV at 400 ℃ and 233 meV at 500 ℃, which is nearly the same as our NEB energy barrier about 231 meV/234 meV. When the external pressure and temperature are increased up to 10 GPa and 400 ℃, respectively, the potential energy of titanium dioxide decreases and its atomic kinetic energy increases. Finally, the transition barrier drops down from 231 meV/234 meV to below 203 meV and the ions in titanium dioxide will easily cross the barrier to transform into α-PbO_2 phase. Considering the fact that the atomic kinetic energy is basically the same as the transition barrier at 500 ℃, the phase transition from α-PbO_2 to rutile phase is very easy to occur at 500 ℃. The reason why there is an error of 50 ℃ between the experimental (450 ℃) and theoretical (500 ℃) temperature may be mainly due to the impure samples used in early studies.

3.3. Temperature and pressure of phase transition

The Gibbs free energy at various temperatures and pressures are calculated for the rutile phase and α-PbO_2 phase of TiO_2 based on Debye's theory.[28] The temperature and pressure conditions of the phase transition between the rutile phase (R) and the α-PbO_2 phase (O) are shown in Fig. 6. Tang and Endo[29] reported that they had not observed the formation of the α-PbO_2 phase at room temperature in experiment, but detected it by heating. There is no intersection of the free energy between these two phases below 100 ℃ in Fig. 6, which also shows that the phase transition cannot occur below 100 ℃ or at room temperature. Jamieson and Olinger pointed out that this transition can occur at 10 GPa and 400 ℃.[27] The pressure required for the rutile phase transiting to the α-PbO_2 phase gradually decreases on heating and there is a significant decrease in the phase transition pressure at 400 ℃ in Fig. 6. Our theoretical transition point (400 ℃, 33 GPa in Fig. 6) also qualitatively conforms to Jamieson and Olinger's observations. The reason for the low experimental phase transition pressure may be due to the impure sample. Tang and Endo[29] reported that it becomes rapid to transform from the rutile phase to the α-PbO_2 phase at more than 750 ℃ in 1993. The transition pressure becomes flat after the temperature has risen more than about 500 ℃ in Fig. 6, which means that no more pressure is needed for the phase transition after the temperature has exceeded 500 ℃ and the transition becomes easier and rapid beyond this temperature. Our lower theoretical temperature may be due to the fact that the volume effect on the phase transition is not considered in our theoretical simulation.

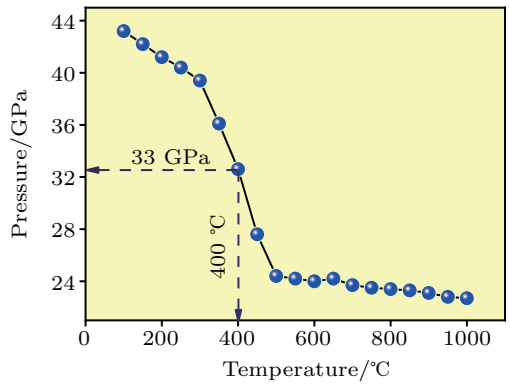


Fig. 6. Temperature and pressure conditions of phase transition between rutile phase (R) and α-PbO_2 phase (O).

4. Conclusions

The martensitic-type phase transformation paths from the rutile phase to the α-PbO_2 phase of TiO_2 are studied with the linear interpolation and NEB/G-SSNEB methods through the first-principles calculations. Our phonon spectra and specific crystallographic correspondences reveal that the titanium atoms of the rutile phase will shuffle along the $[0-11]_{rut}$ crystal direction to form the α-PbO_2 phase. During the phase transition, the oxygen atoms are dragged by the heavier titanium atoms and move along a zigzag path rather than a simple linear path to reach their new equilibrium positions. Our theoretical simulations also reveal that the reverse transition from the rutile phase to the α-PbO_2 phase must be realized easily at above 500 ℃ because the theoretical potential barrier of phase transition is basically the same as the average kinetic energy of molecule unit at 500 ℃. Our theoretical simulations based on Debye theory show that the pressure required for the rutile phase transiting to the α-PbO_2 phase gradually decreases on heating and there is a significant decrease of phase transition pressure at 400 ℃, which qualitatively conforms to those previous experimental observations.

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