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Formation of Anatase Phase in HfO_2 in Tensile Stress: An *Ab Initio* Study

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We report a direct computational evidence of a phase transformation from the baddeleyite phase to an anatase-like phase in HfO_2 with the application of tensile stress. The phase transformation is first order and associated with the shear deformation. The energy–volume calculations indicate that the energetics of the anatase crystal is favorable and the baddeliyite-to-anatase phase transformation occurs -1.0 GPa, implying that the anatase-like phase of HfO_2 can be grown experimentally as thin films under tensile strain.

Hafnia (HfO_2) possesses unique physical properties and can be used for a wide range of applications such as glass–ceramics for planar waveguide, phosphors materials, dielectric materials in optical devices, ceramic, refractory materials, super hard materials, and catalysts and as components in gas sensors and fuel cell electrolytes, due to its thermal stability, high hardness, high permittivity, high refractive index, and large band gap.[1,2] Also, HfO_2 has been recently considered as gate dielectrics with intermediate dielectric constants (k) in the range of 20 to 25. In recent years, HfO_2 has been studied extensively.[3–10]

Hafnia has three polymorphic forms at high temperature and normal pressure conditions: At low temperature, the monoclinic baddeleyite phase (space group $P2_1/c$) is stable.[11] Around 2000 K, there is a first-order displacive martensitic phase transition to a tetragonal structure (space group $P4_2/nmc$).[11] At a temperature of about 2870 K, the tetragonal phase transforms into the cubic fluorite structure (space group $Fm3m$), which in turn melts at 3118 K.[12]

At high pressures, the HfO_2 phase diagram is rather intricate and exhibits many different crystalline phases. HfO_2 undergoes phase transitions to denser structures in the following sequence: $P21/c \rightarrow Pbcm$ ($Pbca$, orthorhombic (OI)) $\rightarrow Pnma$ (orthorhombic (OII)), named cotunnite.[13–15] The phase OII has been confirmed to quench at pressures in excess of 30 GPa.[15]

On the basis that ZrO_2 exhibits a similar crystal structure to HfO_2 and show the same phase transformations at high temperatures. The monoclinic to tetragonal and the tetragonal to cubic phase transformations occur around 1300 and 2700 K, respectively. Both materials show remarkably similar behaviors under pressure and adopt the same high-pressure phases.

At ambient conditions, TiO_2 crystallizes in three modifications: rutile, brookite, and anatase. The high-pressure behavior of TiO_2 has been the subject of many experimental and theoretical investigations.[16,17] At high pressure, the TiO_2 transforms into the monoclinic baddeleyitte structure. In the pressure range of 45–60 GPa, the formation of an orthorhombic phase with space group *Pnma*, is observed in experiments.[17]

Great interest in the high-pressure phases of these materials has also been motivated by the discovery of their superhard cotunnite phase. The crystal structures of these materials at high pressures are also considerably interesting in view of their connection with the pressure-induced phase transitions in SiO_2 because the rutile TiO_2 is expected to undergo sequence phase transformations, similar to that experienced by stishovite SiO_2. Therefore, a better understanding of the high-pressure phase of one of these materials is important not only clarify its phase diagram but also to learn about the evaluation of the other materials at high pressure.

In addition to hydrostatic pressure, studies of the structural and mechanical responses of materials at finite strain are crucial for our understanding of many areas such as phase transformation, theoretical strength, crack propagation, and nanotechnology. Therefore, in this work, we study the response of HfO_2 to tensile stress and predict its low-density anatase-like phase. This finding will provide new perspectives on the phase diagram of HfO_2.

We used the first-principles pseudopotential method within the density functional theory and the generalized gradient approximation of Perdew–Burke and Ernzerhof for the exchange-correlation energy.[18] The calculation was carried out with the *ab initio* program SIESTA[19] using a linear combination of atomic orbitals as the basis set, and norm-conservative Troullier–Martins Pseudopotentials.[20] A split-valence double-ξ plus polarized basis set was used. A uniform mesh with a plane wave cut-off of 150 Ry was used to represent the electron density, the local part of the pseudopotentials, and the Hartree and the exchange-correlation potential. The simulation cell consists of 96 atoms with periodic boundary conditions. We used Γ-point sampling for the Brillouin zone integration. The results were checked with four special k-points but this made almost no variation in the energy (<2 meV) and the volume differences at zero pressure. The system was first equilibrated at zero pressure, and then the tensile stress was gradually increased by an increment of 5.0 GPa. For each value of the stress, the structure was allowed to relax and find its equilibrium volume and lowest energy by optimizing its lattice vectors and atomic positions together until the stress tolerance was <0.5 GPa and the maximum atomic force was smaller than 0.01 eV/Å. For minimization of geometries, a variable-cell shape conjugate-gradient method under a constant pressure was used. For the energy volume calculations, we considered the unit cell for HfO_2 phases. The Brillouin zone integration was performed with automatically generated $6 \times 6 \times 6$ i-point mesh for the phases, following the convention of Monkhorst and Pack.[21] In order to determine the symmetry of the high-pressure phases formed in the simulations, we used the KPLOT program[22] that provides detailed information about space group, cell parameters, and the atomic position of a given structure. For the symmetry analysis, we used 0.2, 4°, and 0.7 Å tolerances for bond lengths, bond angles, and interplanar spacing, respectively. The recent study using different exchange-correlation energy GGA and local den-

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sity approximation (LDA) and different basis shows that the SIESTA *ab initio* code is very successful in predicting the stability, elastic, and electronic properties of HfO_2 (see Ref.[23] for more information).

In order to determine the thermodynamic character of phase transformation, we first study the variation of volume as a function of tensile stress. Figure 1 shows the equation of the state of HfO_2. When the stress is increased from -15 GPa to -20 GPa, the volume suddenly increases, which is characteristic of first-order phase transformation. At this stress, the baddeleyite structure adopts an anatase-like phase as shown Fig. 2. Anatase has the space group $I4_1/amd$ with four HfO_2 formula units in one unit cell. The anatase-like phase consists of sixfold coordinated Hf atoms and threefold coordinated O atoms and each HfO_6 octahedra share corners with four neighbors, and share edges with four other neighbors, forming a zigzag chain with a screw axis. This phase transformation is very simple and associated with the bond breaking between Hf atoms and fourfold coordinated O atoms in the baddeleyite structure.

The baddeleyite to anatase phase transformation is not unusual because the application of hydrostatic pressure produces the same phase transformation in TiO_2.[24] Therefore, understanding the baddaleyite-to-anatase phase transformation in TiO_2 might shed some lights on the phase transformation observed in TiO_2. Therefore, as a next step, we study the pressure dependence of the simulation cell vectors to elucidate the mechanism of this phase change. The variation of simulation cell vectors is presented in Fig. 3. As shown in the figure, the structure is expanded along all directions and the monoclinic β-angle gradually increases to about 117°. We carefully analyze this transformation using the KPLOT program and find that the monoclinic symmetry is preserved until the anatase-like phase is formed.

Next, we study the energy-volume relation of the anatase-like phase to compare its energetic with known phases of HfO_2. The energy–volume data are fitted to the third-order Birch–Murnaghan equation of states and shown in Fig. 4. As expected, the anatase phase lies to the right of the baddeleyite structure on such a plot, in contrast to more common plots involving high-pressure phases that are compressed and lie to the left of baddeleyite. The volume per atom of the anatase phase is expanded by about 21% relative to the baddeleyite phase. The energy difference between the two phases is about 20 meV/atom. This value is less than the energy difference between the baddeleyite state and its high-pressure phase *Pbca* (23 meV/atom) and the energy difference between baddeleyite and its high-temperature tetragonal phase $P4_2/nmc$ (26 meV/atom). This indicates that the energetics of the anatase-like crystal is also favorable.

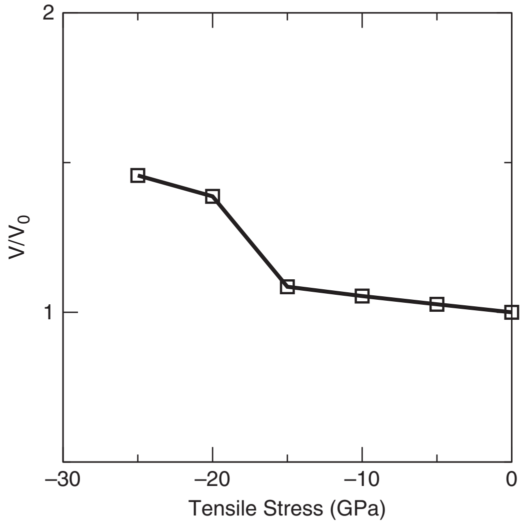

Fig. 1. Volume change as a function of uniaxial stress.

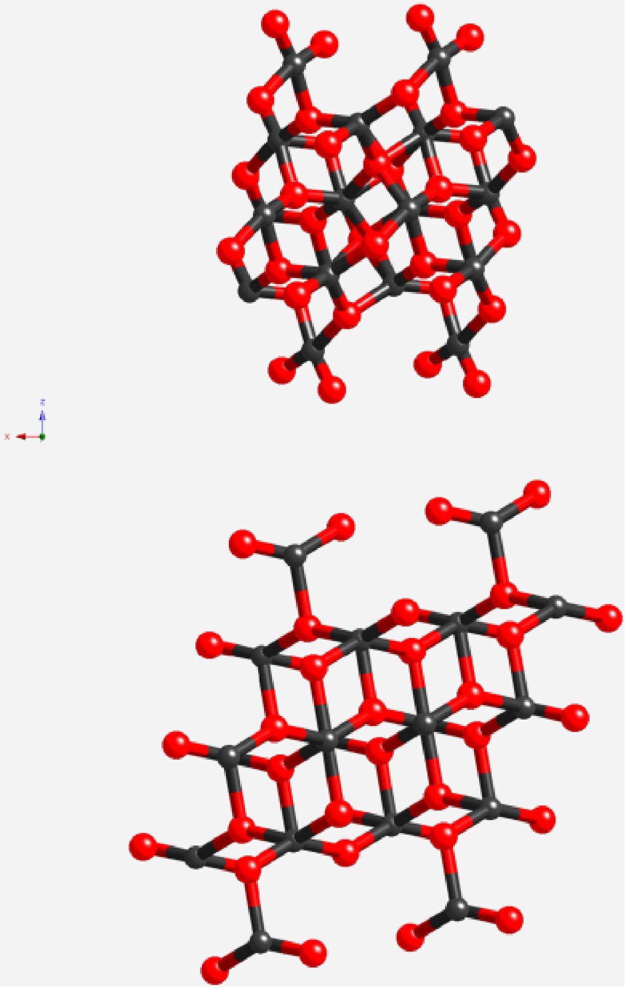

Fig. 2. Crystal structures of HfO_2: *baddeleyite* (top panel) at zero-pressure and anatase-like phase (bottom panel).

From the energy–volume data, we calculate the static enthalpy, $H = E_{tot}+PV$ because at zero temperature the thermodynamically stable phase is the one with the lowest enthalpy. The

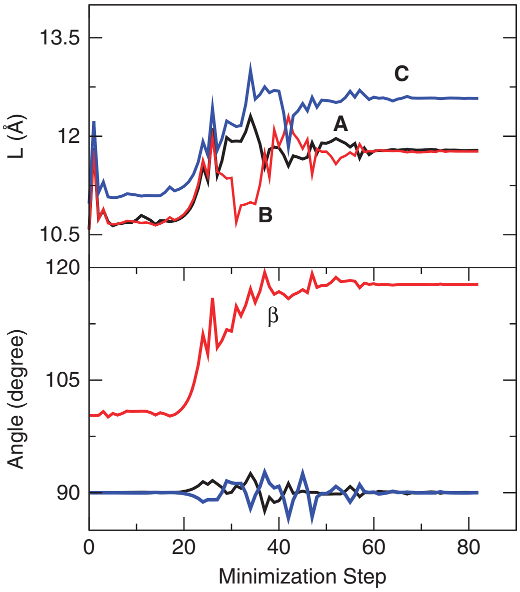

Fig. 3. Change in the simulation cell lengths and angles as a function of pressure. The simulation cell vectors **A**, **B**, and **C** are initially along the [100], [010], and [$\bar{1}$01] directions, respectively. The magnitude of these vectors is plotted in the figure. The β is the angle between **A** and **C** vectors.

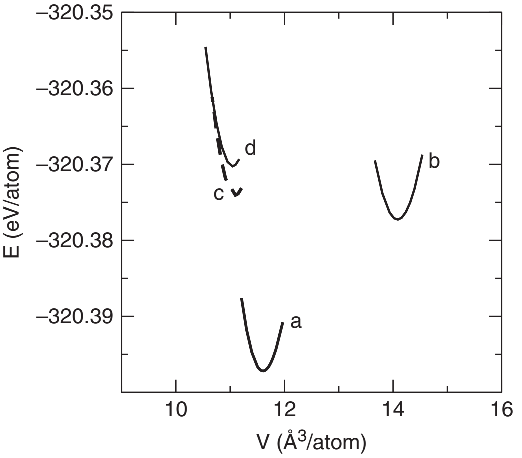

Fig. 4. The computed energy of HfO_2 phases as a function of volume should be the computed energy of HfO_2 (a) baddeleyite (b) anatase (c) *Pbca*, and (d) *P*4_2/*nmc* phases as a function of volume.

crossing of two enthalpy curves indicates a phase transition between these two phases. Figure 5 shows the enthalpy curve of the baddeleyite and anatase phase. Unlike high-pressure phases, where the transformation from one phase to another phase occurs due to pressure, the enthalpy of these two phases is equal only for negative pressure, around −1.0 GPa. There is a significant discrepancy about the magnitude of the critical stress predicted in the constant pressure simulation and the enthalpy calculation. This result is anticipated because of the simulation conditions. The limited box size, the use of periodic boundary conductions, and the lack of defects in the simulated structure affect the critical stress predicted in constant pressure simulations. The periodic boundary conditions lead to an additional coupling of the ions in the simulation box. The lack of any defect in the simulated structure suppresses nucleation and growing. These tend to favor a phase change, in which the entire system undergoes the phase transformation as a collective movement of all ions. As a result, systems have to cross a significant energy barrier to transform from one phase to another one.[25] On the other hand, the thermodynamic theorem does not take into account the possible existence of such an activation barrier separating the two structural phases and provides more reliable information about phase transformations. Therefore, the baddeleyite-to-anatase phase transformation is expected to occur around −1.0 GPa.

In summary, using a constant pressure *ab initio* technique, we predict a phase transformation from the sevenfold coordinated baddeleyite phase to a sixfold coordinated anatase structure in HfO_2 with the application of tensile stress. Comparing the energectic of the anatase phase with that of the other phases of HfO_2, we see that the energetics of the anatase crystal is also favorable. The anatase phase of HfO_2 might offer new applications in technology. The synthesizing of this phase probably cannot be a challenging task for experimentalists and can be growth as thin films under tensile strain. Note that the critical stress of about −1.0 GPa, predicted from the thermodynamics theorem can be attained experimentally.

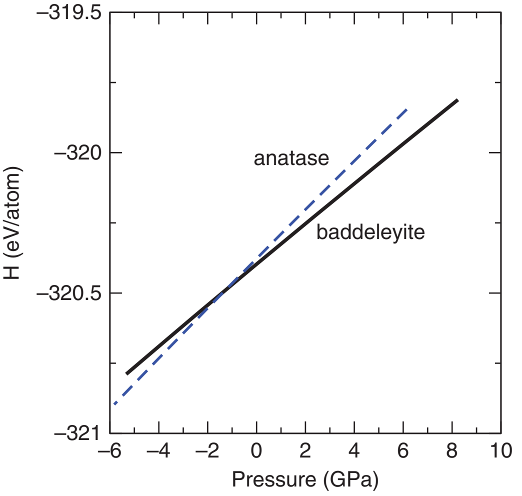

Fig. 5. The calculated enthalpies of HfO_2 structures as a function of pressure.

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