



Master of Philosophy

Analysis of Barium titanate and Hafnium oxide using Phonon Calculation

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Analysis of Barium titanate and Hafnium oxide using Phonon Calculation

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This dissertation is submitted to University of Ulsan in partial fulfillment of The requirements for the degree of *Master of Philosophy in physics*

by

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Department of Physics University of Ulsan July, 2021

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To my loving parents and the love of my life.

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university.

> Sun-Bae Jin July 14, 2021

Abstract

BaTiO₃ has 4 structures. These are cubic $(Pm\bar{3}m)$, orthorhombic (Amm^2) , rhombohedral (R3m), and tetragonal (P4mm). These structures has a constant energy when the k point meshes are 888 (Gamma centered grid). These also has a constant energy when the energy cutoff is around 700 eV. Their the phonon band structures and Gibbs free energies were calculated by DFT and phonon method. The phonon dispersions of $Pm\bar{3}m$, Amm2, R3m, and P4mmare the unstable phases. On the other hand, their stabilities of the phases were measured by a experiment. $Pm\bar{3}m$, Amm2, and P4mm were the unstable phases. R3m was the stable phase. Using the quasi harmonic approximation, I could compute their Gibbs free energies. From their Gibbs free energies, we could get a phase diagram. Temperature has a significant impact on the phase transition. Gibbs free energies of the phases were calculated under the temperatures 0 ~ 500 K at a pressure 0 GPa. The diagram was calculated as orthorhombic \rightarrow tetragonal \rightarrow cubic, and the corresponding transition temperatures are 242 and 391 K, respectively. The rhombohedral structure was computed that the structure did not transform to the orthorhombic structure. The experiment requires that the crystal structure transforms among from the rhombohedral (R3m) to the orthorhombic (Amm2) between 200 and 240 K, then to the tetragonal (P4mm) between 250 and 280 K, and to the cubic $(Pm\bar{3}m)$ between 300 and 320 K.

The phase diagrams and phonon band structures of HfO₂ was calculated for cubic ($Fm\bar{3}m$), monoclinic ($P2_1/c$), tetragonal ($P4_2/nmc$), orthorhombic ($Pca2_1$, Pbca, and Pnma). $Fm\bar{3}m$, $P2_1/c$, and $P4_2/nmc$ belong to the nonpolar phases. These has a constant energy when the k point meshes are 666 (Monkhorst-pack). When the energy cutoff has around 550 eV, they have a constant energy. The orthorhombic phases ($Pca2_1$, Pbca, and Pnma) have a constant energy when the k point meshes are 444 (Monkhorst-pack). When the energy cutoff has around 550 eV, the phases have a constant energy. From the phonon band structures of HfO₂, $Fm\bar{3}m$ and $P4_2/nmc$ are the unstable phases. $P2_1/c$, Pbca, Pnma, and $Pca2_1$ are the stable phases. I got the different result on the phonon dispersion of the orthorhombic phases (Pnma). The reference argued that the orthorhombic phase (Pnma) is the unstable phase. The phase diagram was calculated under the temperatures from 0 to 3000 K and at the pressures between 0 and 30 GPa. The diagram is described the monoclinic ($P2_1/c$) is the most stable at the low temperatures and at the low pressures. When the pressure is from 9 to 15.8 GPa, the orthorhombic (*Pbca*) or the tetragonal ($P4_2/nmc$) are the most stable. When the pressure increases more than 15.8 GPa, the orthorhombic (*Pnma*) is the most stable. This results are similar to their the equilibrium of phase diagram for HfO₂. In addition, when $Fm\bar{3}m$ and $Pca2_1$ consider into the phase diagram, I got the new phase diagram. The cubic phase transforms to the tetragonal at P = 10.1 GPa. The monoclinic phase ($P2_1/c$) is the most stable at the low temperatures and at the low pressures. When the temperature increases, the orthorhombic ($Pca2_1$) or the tetragonal ($P4_2/nmc$) are the most stable. Between the pressures 9 and 15.8 GPa, the orthorhombic (Pbca) is the most stable at the low temperature increases, $P4_2/nmc$ or $Pca2_1$ are the most stable. Also, when the pressure increases more than 15.8 GPa, the orthorhombic (Pnma) is the most stable.

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Chapter 1

Introduction

In this context, there are a harmonic, a quasi harmonic, and an anharmonic approximations for theoretically. These two harmonic sections included theories and results of a phonon calculations. However, the anharmonic part considered only theoretically. I contemplated barium titanate BaTiO₃ (BTO), that represents a perovskite structure. In addition, I considered hafnium oxide HfO₂ (hafnia). The material is known as a high dielectric material. Recently, HfO₂ used in a semiconductor industry. Because the material can make to increase a capacity of semiconductor.

The material BaTiO₃ has four phases. These are cubic $(Pm\bar{3}m)$, orthorhombic (Amm^2) , rhombohedral (R3m), and tetragonal (P4mm) crystal structure. The cubic phase is known as a paraelectric structrue, while the other phases are known as a ferroelectric structures. Also, HfO₂ has five phases. These are cubic $(Fm\bar{3}m)$, monoclinic $(P2_1/c, P2_1/m, Cc, and Pm)$, orthorhombic ($Pca2_1$, $Pmn2_1$, Pbac, and Pnma), tetragonal ($P4_2/nmc$), and triclinic (P1 and $P\bar{1}$) phases. Monoclinic (*Cc*, *Pm*), orthorhombic (*Pca*2₁ and *Pmn*2₁), and triclinic (*P*1) phases have a ferroelectricity. In addition, a phase transition of the BaTiO₃ is known as the cubic $(Pm\bar{3}m)$ transforms to the tetragonal (P4mm), and from the tetragonal to the orthorhombic (Amm2), and to the rhombohedral (R3m). Furthermore, a phase transition of HfO₂ is the monoclinic phase $(P2_1/c)$ transforms to the tetragonal $(P4_2/nmc)$ and the orthorhombic (*Pbca* and *Pnma*). In a computational physics, a scientist often use the density functional theory (DFT) method for analyzing the composition of a material. The method used the Vienna Ab initio simulation package (VASP). This tool deals with the calculation of the first principle (Ab initio). This method used the formulas without considering experiment's values [1]. In addition, a phonon calculation is an important for condensed matter physics. One of the phonon calculations is called phonopy. Phonopy is an open source package for a phonon calculation at harmonic and quasi harmonic levels. In the material science, phonons play a major role in many of the physical properties of condensed matter, such as thermal conductivity and electrical conductivity. I tried to calculate using DFT-VASP and phonopy for BaTiO₃ and HfO₂. In this article, I attempted to compare with a results of several papers [2] [3] [4] [5]. The results contain the phonon band structures, as well as the phase transitions. I considered that are cubic ($Pm\bar{3}m$), orthorhombic (Amm2), rhombohedral (R3m), and tetragonal (P4mm) phases for barium titanate. Also, I considered that are cubic ($Fm\bar{3}m$), monoclinic ($P2_1/c$), orthorhombic ($Pca2_1$, *Pbca*, *Pnma*), and tetragonal ($P4_2/nmc$) phases for hafnium oxide.

Chapter 2

Theoretical Harmonic, Quasi harmonic, and Anharmonic Approximations

2.1 The Harmonic Approximation

I have studied a harmonic, a quasi harmonic, and an anharmonic approximations. First I have focused on a general principles of dynamics of diatomic crystals. In the simple model of a linear chain of atoms, they have a mass m, and located a between each others. They interacted each neighbours. The interaction is represented by

$$E = N\phi(a). \tag{2.1}$$

The energy is in terms of a distance a and the total energy of N atoms. I assume that the move of the number of N atoms and the displacement u of an atom along the chain. The equation (1) denotes that

$$E = N\phi + \sum_{s\geq 1} \frac{1}{s!} \frac{\partial^s \phi}{\partial u^s} \sum_n (u_n - u_{n+1})^2.$$
(2.2)

The equation of a first derivative of ϕ is zero due to the distance *a* is the equilibrium unit cell length when s = 1. Thus, the terms of s = 2 is the first term for first. The term is respect to the harmonic part, and if it handle with more than 2 order, the higher order is respect to the anharmonic terms. Then, we are able to contemplate one dimensional monatomic chain. In this case, the harmonic energy (when s = 2) stands for

$$E_{harmonic} = \frac{1}{2} \frac{\partial^2 \phi}{\partial u^2} \sum_n (u_n - u_{n+1})^2; u_n = \sum_k \tilde{u}_k \exp(i[kx - \omega_k t])$$
(2.3)

where *k* is a wave vector $\frac{2\pi}{\lambda}$ and \tilde{u}_k is the amplitude. In conclusion, the angular frequency that is $\omega_k = (\frac{4J}{m})^{1/2} |\sin(ka/2)|$. Moreover, the formula can expand if the equation considers more interactions in the atoms. It is represented by

$$E = N \sum_{p} \phi_{p}(pa) + \frac{1}{2} \sum_{n,p} (\frac{\partial^{2} \phi_{p}}{\partial u^{2}})_{r_{p} = pa} (u_{n} - u_{n+p})^{2}$$
(2.4)

where *p* is the order of *p*-th atom, and the distance $r_p = pa$. In addition, the harmonic energy with when s = 2 that is $E_{harmonic} = \frac{1}{2} \frac{\partial^2 \phi_p}{\partial r_p^2} \sum_n (u_n - u_{n+p})^2$. Therefore, the angular frequency that is $\omega_k^2 = \frac{4}{m} \sum_p \frac{\partial^2 \phi_p}{\partial r_p^2} \sin^2(\frac{kpa}{2})$. Furthermore, we have to consider that the atoms are each difference. Simply, we can suggest a configuration that are two different atoms's chain with the different force constant *G* and *g*, the mass *M* and *m*, and the displacement *U* and *u*. The harmonic energy that is $E = \frac{1}{2} \sum_n [G(U_n - u_n)^2 + g(u_{n-1} - U_n)^2]$. From the energy, it induces that the solutions of the monatomic chain are that $U_n = \sum_k \tilde{U}_k \exp(i[kna - \omega_k t])$ and $u_n = \sum_k \tilde{u}_k \exp(i[kna - \omega_k t])$. The solutions lead the angular frequency [6]:

$$\omega_k^2 = \frac{(M+m)(G+g)}{2Mm} \pm \frac{((M+m)(G+g) - 16MmGg\sin^2(ka/2))^{1/2}}{2Mm}$$
(2.5)

The angular frequency can deliberate about the different cases. First of all, it is for the long wavelength limit. In this case, the frequency written by

$$\omega_k^2 = \frac{(M+m)(G+g)}{2Mm} \left[1 \pm \left(1 - \frac{2MmGgk^2a^2}{(M+m)^2(G+g)^2}\right)\right]$$
(2.6)

if $k \to 0$ limited, the frequency replace that $\omega_k^2 = \frac{(M+m)(G+g)}{Mm} - O(k^2)$; $\frac{Ggk^2a^2}{(M+m)(G+g)}$. In addition, here is the conditions for the angular frequency:

- For same force constants: $\omega_k^2 = 2G(\frac{1}{M} + \frac{1}{m}); \frac{Gk^2a^2}{2(M+m)}, \omega_k^2 = \frac{2G}{M}; \frac{2G}{m}$ (at the Brillouin zone boundary)
- For same masses: $\omega_k^2 = \frac{2(G+g)}{M}$; $\frac{Ggk^2a^2}{2M(G+g)}$, $\omega_k^2 = \frac{2g}{M}$; $\frac{2G}{M}$ (at the Brillouin zone boundary)
- For equal masses with the force constants $G \gg g$: $\omega_k^2 = \frac{4g}{(M+m)} \sin^2(ka/2)$; $\frac{G(M+m)}{Mm}$

For explaining the atoms move, we have to know a concept of the normal modes and the normal mode coordinates, the displacement equation should represent in three dimensional crystal with monatomic model. The equation is

$$\mathbf{u}(jl,t) = \sum_{\mathbf{k},\mathbf{v}} \mathbf{U}(j,\mathbf{k},\mathbf{v}) \exp(\mathbf{i}[\mathbf{k} \cdot \mathbf{r}(jl) - \boldsymbol{\omega}(\mathbf{k},\mathbf{v})t])$$
(2.7)

where **k** is a wave vector, and *j*-th atom in *l*-th unit cell. The equation (7) can rewrite another form that is $\mathbf{u}(jl, \mathbf{t}) = \frac{1}{(Nm_j)^{1/2}} \sum_{\mathbf{k},v} \mathbf{e}(j, \mathbf{k}, v) \exp(i\mathbf{k} \cdot \mathbf{r}(jl)) \mathbf{Q}(\mathbf{k}, v)$. The vector $\mathbf{e}(j, \mathbf{k}, v)$ is the displacement vector. The quantity $Q(\mathbf{k}, v)$ has a time dependence, also it has a complex scalar. The quantity $Q(\mathbf{k}, v)$ can write by using the reverse Fourier transform of equation.

$$Q(\mathbf{k}, v) = \frac{1}{N^{1/2}} \sum_{jl} m_j^{1/2} \exp(i\mathbf{k} \cdot \mathbf{r}(jl)) \mathbf{e}^*(j, \mathbf{k}, l) \cdot \mathbf{u}(jl, t)$$
(2.8)

The equation is the vibrational modes, also is called the normal modes of the model. The normal modes is orthogonal each others. This means that the modes satisfied the condition [6]

$$\sum_{j} \mathbf{e}(j, \mathbf{k}, v) \cdot \mathbf{e}(j, -\mathbf{k}, v') = \delta_{v, v'}$$
(2.9)

where the value v and v' are the modes. The hamiltonian \mathcal{H} can induce in terms of the quantity $Q(\mathbf{k}, v)$.

$$\mathscr{H} = \frac{1}{2} \sum_{\mathbf{k}, v} \dot{\mathbf{Q}}(\mathbf{k}, v) \dot{\mathbf{Q}}(-\mathbf{k}, v) + \frac{1}{2} \sum_{\mathbf{k}, v} \omega^2(\mathbf{k}, v) \mathbf{Q}(\mathbf{k}, v) \mathbf{Q}(-\mathbf{k}, v)$$
(2.10)

2.2 The Quasi Harmonic Approximation

The quasi harmonic approximation is based on the harmonic approximation. The approximation considers the harmonic approximation from different each volumes. It is volume dependence of phonon frequencies as a sort of anharmonic effects. In addition, it can calculate a thermal expansion and a phase transition. First, we have to contemplate the Helmholtz free energy F. The energy is represented by the quasi harmonic approximation at constant volume V:

$$F(T,V) = E_{lattice}(V) + U_{vibration}(T,V) - TS(T,V)$$
(2.11)

where $E_{lattice}$ is the lattice energy, and $U_{vibration}$ is the vibration energy, *T* is the temperature, and *S* is the entropy. The vibration energy is that

$$U_{vibration} = \frac{1}{N} \sum_{\mathbf{k}, \nu} \left[\frac{1}{2} + n_{\mathbf{k}, i}(T, V) \right] \hbar \omega_{\mathbf{k}, i}(V)$$
(2.12)

where **k** is wave vector in *i*-th band at volume V, and $n_{\mathbf{k},i}$ is the number of (\mathbf{k},i) -phonons. Therefore, the Helmholtz free energy can represent

$$F(T,V) = E_{lattice}(V) + \frac{1}{N} \sum_{\mathbf{k},v} \frac{1}{2} \hbar \omega_{\mathbf{k},i}(V) + \frac{1}{N} \sum_{\mathbf{k},v} k_B T \ln\left[1 - \exp(\Theta_{\mathbf{k},i}(V)/T)\right]$$
(2.13)

where $\Theta_{\mathbf{k},i}(V) = \hbar \omega_{\mathbf{k},i}(V)/k_B$. In addition, the entropy $S = -(\partial F/\partial T)_V$. Therefore, F = U - TS is satisfied. Moreover, if we regard constant pressure, Gibbs free energy is defined at a constant pressure *P*. The minimal value for Gibbs free energy is found at the equilibrium volume for a given temperature and pressure.

$$G(T,P) = \min_{V} \left[U_{vibration}(V) + F(T,V) + PV \right]$$
(2.14)

2.3 The Anharmonic Approximation

The harmonic approximation can not explain some phenomenons. For give an example of the phenomenons, temperature dependence of equilibrium properties, occurrence of phase transitions, and transport properties. These are related with anharmonic interactions. The anharmonic Hamiltonian is that it added anharmonic terms in the harmonic Hamiltonian [6].

$$\mathscr{H} = \frac{1}{2} \sum_{\mathbf{k}, \nu} \dot{\mathcal{Q}}(\mathbf{k}, \nu) \dot{\mathcal{Q}}(-\mathbf{k}, \nu) + \frac{1}{2} \sum_{\mathbf{k}, \nu} \omega_0^2(\mathbf{k}, \nu) \mathcal{Q}(\mathbf{k}, \nu) \mathcal{Q}(-\mathbf{k}, \nu) + \sum_{\kappa > 2} \frac{1}{\kappa!} \sum_{\mathbf{k}_1, \nu_1} \cdots \sum_{\mathbf{k}_{\kappa}, \nu_{\kappa}} V_{\kappa} \begin{pmatrix} \mathbf{k}_1 & \cdots & \mathbf{k}_{\kappa} \\ \nu_1 & \cdots & \nu_{\kappa} \end{pmatrix} \times \mathcal{Q}(\mathbf{k}_1, \nu_1) \cdots \mathcal{Q}(k_{\kappa}, \nu_{\kappa}) \Delta(\mathbf{k}_1 + \mathbf{k}_2 + \cdots + \mathbf{k}_{\kappa})$$
(2.15)

where V_{κ} is the κ -th order coupling constant, $\omega_0(k, v)$ is the harmonic frequency of the mode (\mathbf{k}, v) , and the function $\Delta(\mathbf{G})$ has a value of unity whether **G** is a reciprocal lattice vector.

Chapter 3

Phonon Analysis for Barium titanate and Hafnium oxide

This context explains that the results of the phonon calculations for barium titanate and hafnia. Barium titanate is one of a perovskite structure. The system has a chemical formula ABX₃. The material has four crystal structures. These are cubic $(Pm\bar{3}m)$, orthorhombic (Amm2), rhombohedral (R3m), and tetragonal (P4mm). The cubic phase is a paraelectric structure. The other phases are ferroelectric structures. The phase transition of BaTiO₃ noticed experimentally that is from the cubic to the tetragonal between 300 and 320 K, the tetragonal to the orthorhombic between 250 and 280 K, and the orthorhombic to the rhombohedral around from 200 to 240 K at P=0 GPa [2].

HfO₂ is the high dielectric material. The material has a same structure as ZrO_2 . Hafnia has five structures. This chapter is concentrated on cubic $(Fm\bar{3}m)$, monoclinic $(P2_1/c)$, orthorhombic $(Pca2_1, Pbca, Pnma)$, tetragonal $(P4_2/nmc)$ structures. The low energy of hafnia can classify two ways. Cubic $(Fm\bar{3}m)$, tetragonal $(P4_2/nmc)$, orthorhombic $(Pca2_1)$, monoclinic $(P2_1/c)$ are in nonpolar [3]. Orthorhombic $(Pca2_1)$, monoclinic (Cc, Pm), and triclinic (P1) are belong to polar [3]. The phase transition of hafnia is monoclinic \rightarrow tetragonal \rightarrow orthorhombic. The polar points group can be categorized as the ferroelectric space group [7] by Table 3.1. From the categorization, Amm2, R3m, and P4mm are belong to the ferroelectric space group. $Cc, Pm, P1, Pca2_1$ and $Pmn2_1$ have a ferroelectricity. The structures of BaTiO₃ and HfO₂ are shown in Figure 3.1 and Figure 3.2.

Point group	Space group
C_1	P1
C_2	$P2, P2_1, C2$
C_{1h}	Pm, Pc, Cm, Cc
C	<i>Pmm2</i> , <i>Pmc2</i> ₁ , <i>Pcc2</i> , <i>Pma2</i> , <i>Pca2</i> ₁ , <i>Pnc2</i> , <i>Pmn2</i> ₁ , <i>Pbc2</i> , <i>Pna2</i> ₁ ,
C_{2v}	Pnn2, Cmm2, Cmc2 ₁ , Ccc2, Amm2, Abm2, Ama2, Aba2, Fmm2, Imm2, Iba2 ₁ , Ima2
C_4	$P_4, P4_1, P4_2, P4_3, I4, I4_1$
C	$P4mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$
C_{4v}	$P4_2bc$, $I4mm$, $I4cm$, $I4_1md$, $I4_1cd$
C_3	$P_3, P_{31}, P_{32}, R_{32}$
C_{3v}	P3m1, P31m, P3c1, P31c, R3m, R3c,
<i>C</i> ₆	$P6, P6_1, P6_5, P6_2, P6_4, P6_3$
C_{6v}	<i>P6mm</i> , <i>P6cc</i> , <i>P6</i> ₃ <i>cm</i> , <i>P6</i> ₃ <i>mc</i>

Table 3.1: The ferroelectric space groups.



Figure 3.1: Structures of the material BTO. The green colour is Ba atom, the red is O atom, and the grey is Ti atom. (a) cubic, (b) orthorhombic, (c) rhombohedral, and (d) tetragonal polymorphs.



Figure 3.2: Schematic representation of HfO_2 . These are (a) cubic, (b) monoclinic, (c) orthorhombic, (d) tetragonal phases. The blue colour is Hf atom and the red is O atom.

3.1 Computational method

Density functional theory (DFT) is a computational quantum mechanical modeling method to calculate the ground state energy using an electron density. DTF obtains an approximate solution to the Schrödinger equation of a many body system. The method decreases the computational cost of calculation the ground state wave functions due to the electron density is a function within the three dimensional spatial space while a wave function is a function within the four dimensional space containing the normal spatial coordinates and the spin coordinate.

3.1.1 Hohenberg-Kohn theorem

Hohenberg and Kohn suggested a new method to the many body electron system. The theorem related to any system consisting of electrons moving under the influence of an external potential. They introduced their two theorems.

Theorem 1: The external potential $U_{ext}(\mathbf{r})$ is a unique functional of the electron density $\rho(\mathbf{r})$. The energy functional $E[\rho(\mathbf{r})]$ implied in the first Hohenberg-Kohn theorem can be written in terms of the external potential $U_{ext}(\mathbf{r})$ and where $F[\rho(\mathbf{r})]$ is an unknown.

$$E[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \mathbf{U}_{\text{ext}}(\mathbf{r}) + F[\rho(\mathbf{r})]$$
(3.1)

Theorem 2: The ground state energy can be gotten variationally. The density minimises the total energy is the exact ground state density.

$$E_0 = \min E[\rho(\mathbf{r})] \equiv E[\rho(\mathbf{r})]$$
(3.2)

3.1.2 The local density approximation (LDA)

The functional $E_{xc}[\rho(\mathbf{r})]$ is approximated by the exchange correlation energy of an electron in an homogeneous electron gas of the density $\rho(\mathbf{r})$, the exchange correlation functional for LDA can be written as,

$$E_{xc}^{LDA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho(\mathbf{r})] d\mathbf{r}$$
(3.3)

where $\varepsilon_{xc}[\rho(\mathbf{r})]$ is the exchange correlation energy density of a uniform electron gas with locally computed density $\rho(\mathbf{r})$. The most right data for $\varepsilon_{xc}[\rho(\mathbf{r})]$ is from Quantum Monte Carlo computations. The LDA gives often very good results for a geometrical quantities, a vibrational frequencies, and an energy differences. The principle advantage of LDA-DFT over

Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
Pm3m	4.0358	4.0358	4.0358	90.000	90.000	90.000
Amm2	5.6625	5.7636	4.0446	90.000	90.000	90.488
R3m	4.0000	4.0000	4.0000	89.665	89.665	89.665
P4mm	3.9994	3.9994	4.2288	90.000	90.000	90.000

Table 3.2: The lattice parameter for BaTiO₃ phases.

methods such as Hartree-Fock is that where the LDA many experimentally relevant physical properties can be determined to a useful level of accuracy.

3.1.3 The generalised gradient approximation (GGA)

The generalised gradient approximation (GGA) was suggested to surmount some of the limitation of LDA. The GGA can be represented in terms of an analytic function known as the enhancement factor $F_{xc}[\rho(\mathbf{r}), \nabla(\mathbf{r})]$ that modifies the LDA energy density:

$$E_{xc}^{GGA}\left[\rho(\mathbf{r})\right] = \int \rho(\mathbf{r}) \varepsilon_{xc}\left[\rho(\mathbf{r})\right] F_{xc}\left[\rho(\mathbf{r}), \nabla(\mathbf{r})\right] d\mathbf{r}$$
(3.4)

where $\rho(\mathbf{r})$ is the electronic density and $\nabla(\mathbf{r})$ is the gradient density. The GGA has an especially powerful advantage that it has over the LDA in calculating which the LDA may overvalue by a much as 100 %, whereas the GGA takes an errors of less than 10 %.

3.2 Computational details

The phases of BTO, cubic ($Pm\bar{3}m$), orthorhombic (Amm2), rhombohedral (R3m), and tetragonal (P4mm) structure are calculated by DFT and phonopy. Electronic structure have calculated using density functional theory (DFT). Also, the exchange and the correlation effects are calculated by the Perdew Burke Ernzerhof (PBE) method. Ba atom is used from 'PAW_PBE Ba_sv'. It has 10 valence electrons, and s2p3 for the valence orbitals. The energy of the pseudoatom is 700.8560 eV. Ti atom is used from 'PAW_PBE Ti_pv'. It obtains 10 valence electrons, and d3s1 for the valence orbitals. The energy of the pseudoatom is 1042.5995 eV. O atom used from 'PAW_PBE O'. It contains 6 valence electrons, and s2p4 for the valence orbitals. The energy of the pseudoatom is 432.3788 eV. The lattice parameters are shown in Table 3.2. The lattice parameters of space group $Pm\bar{3}m$ are 4.0358 Å (x-direction), 4.0358Å (y-direction), and 4.0358 Å (z-direction). The cubic phase constructed 90° for all direction. In addition, *Amm2* considered 5.6625 Å (x-direction), 5.7636 Å (y-direction), and 4.0446 Å



Figure 3.3: The convergence for BaTiO₃. Figure 3.3a explains k-point convergence for cubic $(Pm\bar{3}m)$, orthorhombic (Amm2), rhombohedral (R3m), and tetragonal (P4mm). Each of them have a constant energy when k-point meshes 888. Figure 3.3b indicates the energy cutoff convergence. When energy cutoff is around 700 eV, the phases have a constant energy.

(z-direction). The phase structured 90° for all directions. The lattice parameters of R3m are 4.0000 Å (x-direction), 4.0000 Å (y-direction), and 4.0000 Å (z-direction). The rhombohedral structure is made up 89.665° for all directions. The lattice parameters of P4mm are 3.994 Å (x-direction), 3.994 Å (y-direction), and 4.2288 Å (z-direction). The P4mm has 90° for all directions. Next, the k-point meshes (k-points) and the energy cutoff convergences are shown in Figure 3.3. In Figure 3.3a, the x-direction represents k-point meshes and the y-direction symbolizes ground state energy. The x-direction values mean simply k-point meshes, such as the value number 4 intends 4-4-4 k-point meshes and the number 10 represent 10-10-10. The k-point meshes are generated from a Gamma centered grid. When k-point meshes are 888, the cubic phase has a constant energy. The Figure 3.3b describes that the cutoff energy. The x-direction means a value of the energy cutoff and y-direction intends a energy. It converged around 700 eV. Next, the material is HfO₂ and the phases are cubic ($Fm\bar{3}m$), monoclinic $(P2_1/c)$, orthorhombic $(Pca2_1)$, tetragonal $(P4_2/nmc)$. The material was calculated by PBE method. Hf atom used from 'PAW_PBE Hf_sv'. It contains 12 valence electrons and the valence orbitals (5s5p6s5d). The energy of the pseudoatom is 1349.7602 eV. O atom used from 'PAW_PBE O_GW'. It obtains 6 valence electrons and the valence orbitals (s2p4). The energy of the pseudoatom is 432.3788 eV. The lattice parameters of HfO₂ are shown in Table 3.3. The lattice parameters of $Fm\bar{3}m$ are 5.0741 Å (x-direction), 5.0741 Å (y-direction), and 5.0741 Å (z-direction). The phase composed 60° for all directions. The monoclinic phase

Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
$P4_2/nmc$	3.5933	3.5933	5.2247	90.000	90.000	90.000
Pnma	3.3336	5.5564	6.5050	90.000	90.000	90.000
Fm3̄m	5.0741	5.0741	5.0741	60.000	60.000	60.000
$Pca2_1$	5.2659	5.0470	5.0772	90.000	90.000	90.000
Pbca	5.0857	5.2484	10.0588	90.000	90.000	90.000
$P2_{1}/c$	5.1400	5.1897	5.3247	80.325	90.000	90.000

Table 3.3: The lattice parameters for HfO₂ phases.

 $(P2_1/c)$ is made up 5.1400 Å, 5.1897 Å, and 5.3247 Å for each x, y and z-direction, and the phase constructed 80.325° for x-direction , and 90° for y and z-directions. The lattice parameters of $(Pca2_1)$ are 5.1400 Å, 5.1897 Å, and 5.3247 Å. The orthorhombic phase constructed 90° for all directions. In addition, the other orthorhombic phase (Pbca) is consist of 5.0857 Å (x-direction), 5.2484 Å(y-direction), and 10.0588 Å (z-direction). The phase is made of 90° for all directions. Another orthorhombic phase (Pnma), the corresponding lattice parameters x,y, and z are 3.3336 Å, 5.5564 Å, and 6.5050 Å, respectively. The phase structured 90° for all directions. The tetragonal phase $(P4_2/nmc)$ is made up 3.5933 Å, 3.5933 Å, and 5.2247 Å. The phase has 90° for all directions. When k-point meshes (k-points) are 666, the phase has a constant energy for cubic $(Fm\bar{3}m)$, monoclinic $(P2_1/c)$, and tetragonal $(P4_2/nmc)$ phases . The k-point meshes are generated from Monkhorst-pack. Energy cutoff converged around 550 eV for all phases. These are shown in Figure 3.4. The orthorhombic $(Pca2_1, Pbca, Pnma)$ phases converged k-point meshes are at 444. The orthorhombic phases converged around 550 eV for the energy cutoff. Furthermore, k-path of BTO and HfO₂ are shown in Figure 3.5 and Figure 3.6.

3.3 Stability

This section concentrated on a phonon dispersion for the stability of BaTiO₃ phases, such as cubic ($Pm\bar{3}m$), orthorhombic (Amm2), rhombohedral (R3m), and tetragonal (P4mm) phases by $2 \times 2 \times 2$ supersell. The results of the phonon band structures are shown in Figure 3.7. Also, the phases have an electric property. Thus, the phonon band structures have to consider Born effective charge. These phonon dispersions considered a non-analytical term correction. The Figure 3.7 from (a) to (d) describes the phonon dispersions of each phase with the projection density of state at P = 0 GPa. From Figure 3.7 (a), the phonon dispersion indicates that the cubic ($Pm\bar{3}m$) is an unstable because there is the imaginary frequencies. Also, the reference has shown as similar to the band structure [9]. Symmetry points passed



Figure 3.4: The convergence for HfO_2 . These explain k-point mesh convergence and energy cutoff convergence. When k-point meshes are at 666 (the violet line), the energy has a constant for c, m, and t-HfO₂, and o-HfO₂ has a constant energy when k-point meshes are at 444 (the blue line). The k-point meshes generated from Monkhorst-pack. When energy cutoff is around 550 eV, all phases of HfO₂ have a constant energy.



Figure 3.5: The k-path of BTO. These indicates that K-path of BTO. (a) Cubic: $\Gamma = (0, 0, 0)$, R = (0.5, 0.5, 0.5), X = (0, 0.5, 0), M = (0.5, 0.5, 0). (b) Orthorhombic: $\Gamma = (0, 0, 0)$, S = (0, 0.5, 0), R = (0, 0.5, 0.5), Z = (0, 0, 0.5), T = (-0.5, 0.5, 0.5), Y = (-0.5, 0.5, 0). (c) Rhombohedral: $\Gamma = (0, 0, 0)$, L = (0.5, 0, 0), H₀ = (0.5, -0.49476, 0.49476), F = (0.5, 0, 0.5). (d) Tetragonal: $\Gamma = (0, 0, 0)$, X = (0, 0.5, 0), M = (0.5, 0.5, 0), Z = (0, 0, 0.5), R = (0, 0.5, 0.5), A = (0.5, 0.5, 0.5).



Figure 3.6: The k-path for hafnia. These Figures describes that k-path of HfO₂. For instance of the cubic, k-path of each points are $\Gamma = (0, 0, 0), X = (0.5, 0, 0.5), W = (0.5, 0.25, 0.75), L = (0.5, 0.5, 0.5)$. In case of the monoclinic: $Z = (0, 0.5, 0), \Gamma = (0, 0, 0), Y_2 = (-0.5, 0, 0), C_2 = (-0.5, 0.5, 0), D = (0, 0.5, 0.5), B = (0, 0, 0.5)$. The orthorhombic: $Z = (0, 0, 0.5), \Gamma = (0, 0, 0), Y = (0, 0.5, 0.5), \Gamma = (0, 0, 0.5), U = (0.5, 0.5), O = (0, 0, 0.5), C = (0.5, 0.5, 0.5), U = (0.5, 0.5), U = (0.5, 0.5), C = (0.5, 0.5, 0.5), C = (0.5, 0.5, 0.5), C = (0.5, 0.5), C =$

through $\Gamma - X - M - \Gamma - R - M$ 3.5. (b) The orthorhombic phase is not a stable due to the negative frequency, as shown by Amm2 phonon dispersion. The negative frequency appeared between points Γ and S, and between Y and Γ (K-path: $\Gamma - S - R - Z - T - Y - \Gamma$) 3.5. (c) The phonon band structure for R3m is described as unstable because of the imaginary frequency. On the other hand, the reference indicated that the rhombohedral (R3m) phase is a stable [8] [10–13]. The tetragonal (P4mm) phase is an unstable, because the band structure has the negative frequency as well as the phonon band structure of the reference [14]. K-path: $\Gamma - X - M - \Gamma - Z - R - A - Z|X - R|M$ 3.5. In case of HfO₂ is considered for 2 × 2 × 2 supersell. These are cubic $(Fm\bar{3}m)$, monoclinic $(P2_1/c)$, orthorhombic $(Pca2_1, Pbca, Pnma)$, tetragonal $(P4_2/nmc)$. The phonon band structures and the projection density of state for hafnia are shown in Figure 3.8. The Figure 3.8 (a) is the phonon dispersion of the space group $Fm\bar{3}m$. The symmetry points considered in $\Gamma - X - W - L - \Gamma$. The phonon band structure of $Fm\bar{3}m$ has a valley at X point. However, the experiment results shows the valley at L points. It demonstrates that the structure of phonon bands differs from their phonon dispersion. [15]. Although the valley placed the different position, both the phonon dispersions indicate that $Fm\bar{3}m$ is an unstable. (b) $P2_1/c$ is a stable. The reason for this is that the imaginary frequency does not exist. The phonon method seems to be similar to the one used in the reference [15]. The k-path of $P2_1/c$ contemplated in $Z - \Gamma - Y - C - D - B - \Gamma$. (c) The band struc-



Figure 3.7: The BTO phonon band structures and projection density of states at P = 0 GPa. From (a) to (d), these indicate that the phonon dispersions and involved the projection density of state. We can notice the stability from the phonon dispersions. (a) is the cubic phonon dispersion. The cubic $(Pm\bar{3}m)$ phase has an imaginary frequency. It means that the phase is unstable. The other phases, the orthorhombic (Amm2) and the tetragonal (P4mm) are unstable phases. Also, the rhombohedral (R3m) is unstable phase. However, R3m was calculated as stable by their computations [8].



Figure 3.8: The phonon band structures and projection density of states for HfO₂ at P = 0 GPa. These are the phonon dispersions for HfO₂ phases by phonony. (a) Cubic $(Fm\bar{3}m)$ and (c) tetragonal $(P4_2/nmc)$ phases of phonon dispersions have imaginary frequency. The band structures intend that $Fm\bar{3}m$ and $P4_2/nmc$ are unstable due to the imaginary frequency. Phonon band structures (b) monoclinic $(P2_1/c)$ and (d) orthorhombic (Pbca), (e) orthorhombic (Pnma), and (f) orthorhombic $(Pca2_1)$ have no imaginary frequency. Thus, $P2_1/c$, Pbca, Pnma, and $Pca2_1$ are stable.

ture shows that the $P4_2/nmc$ is an unstable due to the imaginary frequency. The reference [15] argued the tetragonal structure is unstable. (d) The orthorhombic phase (*Pbca*) is a stable. Because there is not the imaginary frequency. (e) *Pnma* is a stable, and the imaginary frequency does not exist. However, their result of the phonon dispersion of *Pnma* argued that the phase is not a stable. There is the imaginary frequency at Γ point [15]. The two orthorhombic phase (*Pbca* and *Pnma*) of k-path considered in $Z - \Gamma - Y - T - U - X - \Gamma$. (f) The phonon dispersion of *Pca2*₁ describes that the phase is a stable. The phonon band structure by the reference has same result that *Pca2*₁ is a stable [15]. In addition, the phonon dispersions contemplated the non-analytical term correction.

3.4 Quasi harmonic approximation

The quasi harmonic approximation is used for volume dependence of phonon frequencies as a part of anharmonic effect. A part of the temperature effect can be included into total energy of electronic structure through phonon Helmholtz free energy at constant volume (Equation 2.13). The equation can transform from function of V to function of P (Equation 2.14). The right terms of the equation means to find a unique minimum value in the brakets by a changing volume. The quasi harmonic approximation indicates volume dependent thermal effects. From the results of properties by the phonon calculation, thermal expansion and heat capacity at a constant pressure can be calculated under the approximation [6]. The method suggests five volume points to run for volume fitting at least. The results of the quasi harmonic approximation for c-HfO₂ ($Fm\bar{3}m$) is shown in Figure 3.9. Left side of picture describes the volume fitting versus free energy for cubic $(Fm\bar{3}m)$. This approximation should contemplate different volumes of phase. In Figure 3.9, there are six blue points. The points represent the different volumes of cubic $(Fm\bar{3}m)$. The each volume point are original volume (V_0) , plus-minus two percent $V_0 \pm 2$ %, $V_0 \pm 4$ %, and $V_0 \pm 6$ % points. The red points mean that the minimum volume from 0 to 3000 K. The original volume is 32.70 Å. The volume is generated by a parameter of $Fm\bar{3}m$ in Table 3.3. In addition, the approximation gives the information that is relation with a temperature (K) and a volume $(Å^3)$, and a temperature (K) versus a thermal expansion (K^{-1}) . These are calculated from the temperature is 0 to 3000 K at a pressure 0 GPa. In addition, it was also expanded to compute Gibbs free energy for BaTiO₃ and HfO₂ under varied pressures.

First of all, Gibbs free energy for the BaTiO₃ phases was calculated at P = 0 GPa with the temperatures $T = 0 \sim 500$ K. It is shown in Figure 3.10. There are two phase transitions. As the experiment, the effect of temperature for phase transition is known as R3m to Amm2, then to P4mm, and to $Pm\bar{3}m$. On the other hand, the rhombohedral (R3m) did not transform to the



Figure 3.9: The results of the quasi harmonic approximation for c-HfO₂ ($Fm\bar{3}m$). The results involved a volume fitting, a relation of temperature and volume, and temperature versus a thermal expansion at P=0 GPa for c-HfO₂. The computation should contemplate more than five points. The points used original volume (V_0) point, $V_0 \pm 2$ % points, $V_0 \pm 4$ % points, and $V_0 \pm 6$ % points. From the volume points, these can obtain a thermal properties, such as temperature vs volume and temperature vs thermal expansion.

orthorhombic (*Amm*2). The diagram shows that R3m is the most stable under the temperatures from 0 to 500 K. The reason is that the phonon band structure for R3m has a problem. R3mhas to be stable, but Figure 3.7 (c) described the phase is not stable structure. As the result raised that the rhombohedral did not phase transform. Although, R3m did not phase transform to *Amm*2, the sequence of the temperature induced the phase transitions are the orthorhombic (*Amm*2) transformed to the tetragonal (*P*4*mm*) around 242 K, and then to the cubic (*Pm* $\bar{3}m$) around 391 K. The reference [2] reported the phase transitions that are from R3m to *Amm*2 between 200 and 240 K, then to *P*4*mm* between 250 and 280 K, and to *Pm* $\bar{3}m$ between 300 and 320 K. Their results demonstrate that the temperatures of phase transitions are different to the temperatures (Figure 3.10). Because they calculated the phase transitions by using the PBE0 functional.

Second, Gibbs free energies for the HfO₂ phases calculated at temperatures *T* between 0 and 3000 K and under pressures *P* from 0 to 30 GPa. It is shown in Figure 3.11. Figure 3.11 shows Gibbs free energy at different pressures *P* for the phases. These describe the phase-transition about the temperatures $T = 0 \sim 3000$ K and at pressure 0, 3, 6, and 9 GPa. In Figure 3.11 (a), the monoclinic $(P2_1/c)$ is the most stable phase at T = 0 K. At P = 0 GPa, the phase transition occurred that the cubic $(Fm\bar{3}m)$ to the orthorhombic $(Pca2_1)$ around 2057 K, the orthorhombic phase transforms to the monoclinic $(P2_1/c)$ around 2001 K. When P = 3 GPa, the cubic $(Fm\bar{3}m)$ phase transformed to the orthorhombic $(Pca2_1)$ around 1800



Figure 3.10: The Gibbs free energy for BaTiO₃ phases. Computed Gibbs free energy by an increasing temperature (0 ~ 500 K) at a pressure of 0 GPa. The sequence of the phase transitions is orthorhombic (*Amm2*) \rightarrow tetragonal (*P4mm*) \rightarrow cubic (*Pm*3*m*) and the corresponding transition temperatures are 242 and 391 K, respectively. The rhombohedral (*R3m*) did not transform to the orthorhombic (*Amm2*). *R3m* is the most stable under the temperatures *T* = 0 ~ 500 K.



Figure 3.11: The Gibbs free energy for HfO₂at different pressures *P*. Calculated Gibbs free energy by temperatures $T = 0 \sim 3000$ K when the different pressures have P = 0 GPa, P = 3 GPa, P = 6 GPa, and P = 9 GPa. The purple colour line is the cubic (*Fm*3*m*). The green line is the monoclinic (*P*2₁/*c*), The sky blue line is the tetragonal (*P*4₂/*nmc*), the yellow line is the orthorhombic (*Pca*2₁), the red line is the orthorhombic (*Pbca*), and the blue line is the orthorhombic (*Pnma*). The most stable phase is the monoclinic (*P*2₁/*c*) at T = 0 K and P = 0 GPa. Phase transition: cubic (*Fm*3*m*) to orthorhombic (*Pca*2₁), then to monoclinic (*P*2₁/*c*) at P = 0, 3, 6, and 9 GPa.



Figure 3.12: The equilibrium of phase diagram for HfO₂. The phase diagrams are made by the phase transition points using the relation of Gibbs free energy for different the phases. The diagram considered from the low temperatures to the high temperatures (0 ~ 3000 K) and contemplated from the low pressures to the high pressures (0 ~ 30 GPa). Figure 3.12a included tetragonal ($P4_2/nmc$), monoclinic ($P2_1/c$), and orthorhombic (Pbca and Pnma). Figure 3.12b just added the cubic ($Fm\bar{3}m$) phase and the orthorhombic ($Pca2_1$) phase in the left figure. When the nonpolar monoclinic ($P2_1/c$) phase is at the low temperatures and the low pressures, the phase is most stable. In addition, when the phase diagram considers the high temperatures and the high pressures, the orthorhombic phase (Pnma) is the most stable.

K and then to the monoclinic $(P2_1/c)$ around 1014 K (Figure 3.11 (b)). When P = 6 GPa, the phase transitions: $Fm\bar{3}m$ to $Pca2_1$ around 1604 K, then to $P2_1/c$ around 373 K (Figure 3.11 (c)). When P = 9 GPa, the phase transitions: $Fm\bar{3}m$ to $Pca2_1$ around 1449 K, then to $P2_1/c$ around 290 K (Figure 3.11 (d)). Furthermore, it is expanded to investigate how the material phase transforms under pressures P from 0 to 30 GPa. The phase diagram of HfO_2 is shown in Figure 3.12. The phase diagrams explain an equilibrium of phase for HfO_2 . Figure 3.12a included the tetragonal $(P4_2/nmc)$, the monoclinic $(P2_1/c)$, the orthorhombic (*Pbca* and *Pnma*). The monoclinic phase $(P2_1/c)$ is the most stable at the low temperatures and the low pressures. Between 9 and 15.8 GPa, the orthorhombic phase (Pbca) is the most stable at the low temperatures (0 ~ 1150 K). The tetragonal phase $(P4_2/nmc)$ is the most stable at the high temperatures. In addition, when the pressure increases more than 15.8 GPa, the orthorhombic (Pnma) phase the is most stable. From the reference, the computed Gibbs free energy with temperature for nonpolar the tetragonal $(P4_2/nmc)$ phase by phonopy did not transform to the monoclinic phase $(P2_1/c)$ under the pressures $P = 0 \sim 4$ GPa. The computed equilibrium phase diagram [3] indicated that $P4_2/nmc$ transforms to $P2_1/c$ under the pressures $P = 0 \sim 10$ GPa. The reference was argued that *Pbca* is the most stable the pressures between 10 and 20 GPa with the temperatures 0 ~ 2500 K. The tetragonal phase $(P4_2/nmc)$ is the most stable at over 2400 K when the pressures are from 0 to around 20 GPa. And *Pnma* the is most stable when the pressure increases more than 19 GPa [3]. The phase diagram (Figure 3.12a) is similar to their phase diagram [3]. In addition, two phases ($Fm\bar{3}m$) and $Pca2_1$) added in the Figure. Another phase diagram is shown in Figure 3.12b. $Fm\bar{3}m$, $P4_2/nmc$, $P2_1/c$, Pbca, and Pnma are affiliated with the nonpolar structure. $Pca2_1$ belongs to the polar phase. The orthorhombic $(Pca2_1)$ phase is known as a stable phase when the phase doped. The orthorhombic phase is known that HfO₂ may adopt two other orthorhombic metastable phases ($Pca2_1$ and $Pmn2_1$) over a wide range of pressures and temperatures [3]. On the other hands, I used the orthorhombic phase $(Pca2_1)$ without doping. Because the phonon band structure shows that the phase is a stable (Figure 3.8 (c)). The reference equilibrium of phase diagram for hafnia considered the ferroelectric phases (Pca21 and Pnm21). However, I considered only $Pca2_1$. From Figure 3.12b, the monoclinic phase $(P2_1/c)$ is the most stable when the temperatures consider under $0 \sim 2000$ K and the pressures are between 0 and 9 GPa. The cubic phase $(Fm\bar{3}m)$ transforms to the tetragonal phase $(P4_2/nmc)$ at the pressure P =10.1 GPa. Then, the tetragonal phase transforms to $Pca2_1$ under the pressures P from 10.1 to 15.9 GPa. When the temperatures are low $(0 \sim 1150 \text{ K})$, the orthorhombic phase (*Pbca*) is the most stable. Then, when the temperature increases, the orthorhombic phase $(Pca2_1)$ or the tetragonal $(P4_2/nmc)$ are the most stable. Furthermore, when the pressure increases more than 15.8 GPa, the orthorhombic phase (*Pnma*) is the most stable. The phase diagram showed that is similar to their results in its totality [3].

Chapter 4

Conclusion

Using the phonon technique and density functional theory (DFT), the phase diagrams and phonon band structures of BaTiO₃ and HfO₂ are computed. BTO has four phases. The phases are cubic ($Pm\bar{3}m$), orthorhombic (Amm2), rhombohedral (R3m), and tetragonal (P4mm). These structures have relaxed when the k-point mesh at 888 (Gamma centered grid), and the energy cutoff is around 700 eV. Compared to the reference with respect to the phonon band structure, phonon calculation indicates that $Pm\bar{3}m$, Amm2, R3m, and P4mm are an unstable. However, the reference showed that the rhombohedral phase (R3m) is a stable [8] [10–13]. Because the rhombohedral (R3m) is calculated by $2 \times 2 \times 2$ supersell, but they calculated larger than $2 \times 2 \times 2$ supersell. In addition, the phase transition of BaTiO₃ was calculated orthorhombic \rightarrow tetragonal \rightarrow cubic and the corresponding transition temperatures are 242 and 391 K, respectively. The rhombohedral (R3m) has to transform to the orthorhombic (Amm2). However, R3m did not transform to Amm2. Because the phonon dispersion for R3m is an unstable (Figure 3.7 (c)). As the experiment, the rhombohedral phase is a stable structure. Because of the unstable phase, R3m did not phase transform to Amm2.

Second, HfO₂ has five phases. The phases can be categorized a nonpolar and a polar. This phonon calculations focused on the nonpolar phases that are cubic $(Fm\bar{3}m)$, monoclinic $(P2_1/c)$, tetragonal $(P4_2/nmc)$, orthorhombic (Pbca and Pnma). The polar phase is orthorhombic $(Pca2_1)$. The nonpolar phases $(Fm\bar{3}m, P2_1/c, \text{ and } P4_2/nmc)$ considered the k-point meshes are 666 (Monkhorst-pack) and the energy cutoff considered around 550 eV. In addition, the orthorhombic phases $(Pbca, Pnma, \text{ and } Pca2_1)$ contemplated the k-point meshes are 444 (Monkhorst-pack) and the energy cutoff is around 550 eV. The phonon dispersions of hafnia indicates that $P2_1/c$, Pbca, Pnma, and $Pca2_1$ are the stable phases, while the phases $Fm\bar{3}m$ and $P4_2/nmc$ are the unstable phases. Also, the reference was argued the materials, $P2_1/c$, Pbca, Pnma, and $Pca2_1$ are the stable phases, and $Fm\bar{3}m$ and $P4_2/nmc$ are the unstable phase. However, the orthorhombic phase (Pnma) was measured as the unstable phase [15].

The phonon dispersion of *Pnma* was described that the phase is the stable phase (Figure 3.8 (e)). The reason is that it is estimated by the different supercell size and it was used the different the number of electrons on DFT calculation. The phase transition (Figure 3.11) describes the cubic $(Fm\bar{3}m)$ to the orthorhombic $(Pca2_1)$ around 2057 K and to the monoclinic $(P2_1/c)$ around 2001 K at P = 0 GPa. However, the tetragonal $(P4_2/nmc)$ has not phase transition to the monoclinic phase $(P2_1/c)$ at P = 0 GPa. From Figure 3.12, it deduced the monoclinic phase $(P2_1/c)$ is the most stable at the pressures P from 0 to 9 GPa. When the pressure increases until 15.8 GPa, the orthorhombic phase (*Pbca*) or the tetragonal phase ($P4_2/nmc$) are the most stable. In addition, when the pressure increases more than 15.8 GPa, the orthorhombic phase (*Pnma*) is the most stable. From the reference [3], the tetragonal ($P4_2/nmc$) phase transformed to the monoclinic phase $(P2_1/c)$ at 0 to around 10 GPa. However, the phase diagram 3.12a describes that $P4_2/nmc$ transformed to $P2_1/c$ between $P = 5 \sim 9$ GPa. When the pressure is increasing, the two orthorhombic phases (Pbca or Pnma) are the most stable. The phase diagram is similar to their diagram [3]. Furthermore, the new phase diagram (Figure 3.12b) demonstrated that $P2_1/c$ is the most stable between 0 and 9 GPa at low temperatures. When the temperature increases, $Pca2_1$ or $P4_2/nmc$ or $Fm\bar{3}m$ are the most stable. Moreover, when the pressures are in 9 ~ 15.8 GPa, Pbca is the most stable at the low temperatures. When the temperature increases, $Pca2_1$ or $P4_2/nmc$ are the most stable. If the pressure increases more than 15.8 GPa, *Pnma* is the most stable.

[6] [3] [15] [4] [5] [2] [9] [7] [10–13] [8] [14][1]

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