INVESTIGATION OF PROPERTIES IN BARIUM CHALCOGENIDES FROM FIRST-PRINCIPLES CALCULATIONS

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Summary

Structural and electronic properties of barium chalcogenides were systematically studied using first-principles calculations based on the generalized gradient approximation and/or local density approximation methods. The calculated band structures showed that all barium chalcogenides are direct band-gap semiconductors. Both conduction and valence bands in compounds are formed by the valence electrons of the group VI elements. Meanwhile, the calculated energy gaps of barium chalcogenides follow two linear relationships with $1/a^2$ ($a$ is the lattice constant) depending on whether oxygen is a constituent element. These results are in agreement with the experimental observations for binary barium chalcogenides reported in literatures. Moreover, besides energy gaps, all calculated electronic properties of barium chalcogenides containing oxygen seem to obey a trend different from that of the compounds not containing oxygen. This behavior is further explained according to the special chemical bonds of Ba–O. Pauling electronegativity shows that ionic bonds are strong in Ba–O but weak in others (bonds between the barium and one of the group VI elements). Hence, when oxygen is introduced into barium chalcogenides, the valence electrons would be restricted by the oxygen atoms, which results in a high charge density near the oxygen atoms and influences the electronic properties of the compounds. Finally, energy gaps of barium chalcogenides can be greatly adjusted by introducing oxygen. These results might be useful for gap-tailoring of semiconductors.

Meanwhile, the behavior of oxygen on a BaTe(111) surface was further studied by
first-principles methods. Both the molecular dynamics and Broyden-Fletcher-Goldfarb-Shano running were employed for surface structure optimization. During the calculations, convergence tests were performed compulsorily with regard to vacuum size, the number of layers, cutoff energy, and k points. The first two tests were to reduce the scale of supercell and the interactions between two surfaces in the supercell. The last two tests were to choose corresponding computational parameters. In the studied system of oxygen on a BaTe(111) surface with or without defects, supercells with seven-layer atoms and a vacuum of 9 Å were found to meet all basic requirements. In the total-energy calculations, a cutoff energy of 500 eV and 9 k points were necessary. An oxygen atom on a clear BaTe(111) was first studied. There are four possible sites for oxygen to sit on the BaTe(111). The calculated surface energies showed that oxygen prefers site 3 (4Ba site in Fig. 4.3). Finally, the theoretical surface energies calculated using the supercells with various defects in the BaTe(111) surface showed that a vacancy or oxygen atom on a tellurium site is stable in the Ba-rich BaTe(111) surface while a vacancy or tellurium atom on a barium site is stable in the Te-rich BaTe(111) surface. The results indicate that the oxygen atom is possible to occupy the tellurium site in a Ba-rich BaTe(111) surface. It is, therefore, possible to tailor the gap properties of II-VI semiconductor by diffusing oxygen on a BaTe(111) surface in the future.
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List of Symbols and Abbreviations

ASW  
augmented spherical wave

BFGS  
Broyden-Fletcher-Goldfarb-Shano

BZ  
Brillouin zone

CASTEP  
Cambridge serial total energy package

DFT  
density-functional theory

DOS  
density of state

FP-LMTO  
full-potential linear muffin-tin-orbital

GGA  
generalized gradient approximation

HF  
Hartree-Fock

HF-PW  
Hartree-Fock Perdew-Wang

HF-PZ  
Hartree-Fock Perdew-Zunger

LAPW  
linearized augmented plane wave

LC  
lattice constant

LDA  
local density approximation

MD  
molecular dynamics

PDOS  
partial density of state

PWP  
plane-wave pseudopotential
List of Publications

Chapter 1: Introduction and Literature Review

II-VI chalcogenide compounds have attracted increasing interest due to their potential applications in light-emitting diodes (LEDs) and laser diodes (LDs). After the first demonstration of a blue-green-emitting laser using ZnSe by Haase et al. in 1991, many experimental and theoretical results have been reported for chalcogenides such as zinc chalcogenides, cadmium chalcogenides, and beryllium chalcogenides. It is expected that chalcogenides will be potential candidates, complementing the well-known IV and III-V semiconductors, to fabricate new electrical and optical devices. On the other hand, the group VI elements experience a change from non-metal (oxygen or sulphur) to metal (tellurium or polonium), which provides a good system for the analysis of general chemical trends among chalcogenides, as demonstrated in recent publications such as lead, tin, and antimony chalcogenides.

Until now, only a few reports on first-principles calculations are available in the study of the pressure-induced phase transformation in barium chalcogenides. No systematic research on the electronic properties of barium chalcogenides was reported, although these compounds may lead to some unique optoelectronic properties due to their diverse bond characteristics. A systematic study of electronic properties in barium compounds may not only enrich the fundamental understanding of barium chalcogenides, but also complement the research on all chalcogenides. The obtained relationship between electronic properties and chemical bonds may be further used in...
the design of wide-band-gap II-VI semiconductor for various applications, such as blue-emitting lasers.

In the following section, recent theoretical results from first-principles calculations for alkaline earth chalcogenides, including barium chalcogenides, are briefly summarized in terms of the phase transformation, bulk modulus, cohesive energy, band structure, density of state (DOS), energy gap, charge density, and elastic constant.

1.1 Theoretical Development in II-VI Alkaline Earth Chalcogenides

1.1.1 Equilibrium Volume, Transition Pressure, and Bulk Module

Almost all alkaline earth chalcogenides experience a pressure-induced phase transition, such as from a structure of B1 (NaCl type, \( F_{\text{m} \bar{3} \text{m}} \), space group of 225) to B2 (CsCl type, \( P_{\text{m} \bar{3} \text{m}} \), space group of 221), and followed by a metallization phenomenon.\(^{13-18}\) Due to their high-symmetry structures and small coordination numbers, the alkaline earth chalcogenides are often employed to study the pressure-induced phase transition and metallization.

According to the thermodynamic theorem, a phase transition would occur when the Gibbs free energies of transition phases are equal. Gibbs free energy is defined as \( G = E_{\text{tot}} + pV - TS \), where \( G \) is the Gibbs free energy, \( p \) is the pressure, \( V \) is the volume, \( T \) is the temperature in Kelvin and \( S \) is the entropy of a system. \( E_{\text{tot}} \) is the total energy and can be obtained from a first-principles calculation. For a transition between phase \( A \) and \( B \) at 0 K, we have
\[ G_A = E_{tot}^A + p_t \times V_A - 0 \times S_A = E_{tot}^A + p_t \times V_A = H_A \]  \hspace{1cm} 1.1

and

\[ G_B = E_{tot}^B + p_t \times V_B - 0 \times S_B = E_{tot}^B + p_t \times V_B = H_B , \]  \hspace{1cm} 1.2

where \( p_t \) is the transition pressure, \( H \) is the enthalpy, \( A \) and \( B \) are the studied phases.

During the phase transition, \( G_A = G_B \). Then, Eqs. 1.1 and 1.2 can be simplified as

\[ p_t = \frac{E_{tot}^A - E_{tot}^B}{V_A - V_B} = -\frac{\Delta E_{tot}^{A\leftrightarrow B}}{\Delta V_{A\leftrightarrow B}} . \]  \hspace{1cm} 1.3

The equation indicates that the pressure-induced phase transition occurs along the common tangent line between the \( E_{tot}(V) \) curves of the transition phases under consideration. The negative slope of the common tangent line is the transition pressure \( p_t \).

Using various theoretical methods, the total energies at different volumes can be calculated. Then, the results of total energy are fitted to the Birch-Murnaghan’s equation\(^{19,20}\) and obtain the equilibrium volume, bulk modulus, and its pressure derivative in materials. The Birch-Murnaghan’s equation is written as\(^{21,22}\)

\[
E(V) = B_0 V_0 \left[ \frac{1}{B'(B'-1)} \left( \frac{V_0}{V} \right)^{B'-1} + \frac{1}{B'} \frac{V}{V_0} - \frac{1}{B'-1} \right] + E_0 .
\]  \hspace{1cm} 1.4

The third-order Birch-Murnaghan’s equation of state is\(^{23,24}\)

\[
E(V) = -\frac{9}{16} B_0 \left[ (4-B') \frac{V_0^3}{V^2} - \left( 14 - 3B' \right) \frac{V_0^{7/3}}{V^{4/3}} + \left( 16 - 3B' \right) \frac{V_0^{5/3}}{V^{2/3}} \right] + \text{const} ,
\]  \hspace{1cm} 1.5

where \( E_0, V_0, B_0, \) and \( B' \) are the equilibrium total energy, the equilibrium volume, the bulk modulus, and the pressure derivative of bulk modulus at the equilibrium volume, respectively.
Another important equation for studying the phase transition is

\[ P = -\frac{\partial E_{\text{tot}}}{\partial V}. \]  

This equation indicates that the pressure applied to materials is obtained by taking the volume derivative of the total energy. The bulk modulus in materials can be described as

\[ B = -V_0 \frac{\partial P}{\partial V} = V_0 \frac{\partial^2 E_{\text{tot}}}{\partial V^2}. \]

After the phase transition, a metallization usually occurs in alkaline earth chalcogenides, which is characterized by an overlap of the conduction and valence bands in band structures. During the theoretical calculations, the energy gaps are calculated under various pressures. The metallization happens when the energy gap is equal to zero and the pressure at this point is called as the metallization pressure. So far, a lot of papers have been published for theoretical studies of the phase transitions and metallization of alkaline earth chalcogenides. Some results are summarized in TABLES 1.1-1.3.21,25-36

TABLES 1.1-1.3 show that, although a number of first-principles methods were conducted to study the properties in alkaline earth chalcogenides, it is still a great challenge to get the theoretical results agreeing well with experiments, such as bulk modulus. One of the possible reasons is that a lot of approximations are used in every first-principles formalism. For example, in the local density approximation (LDA) or generalized gradient approximation (GGA) method, the representation of the exchange-correlation energy in the Kohn-Sham equation (Kohn-Sham equation will be introduced in the next section.) is only theoretically assumed. Nevertheless, it is
### TABLE 1.1 Equilibrium lattice constants (Å) of alkaline earth chalcogenides.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Theoretical Results</th>
<th>Experimental Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>4.2287, (^a) 4.3446, (^b) 4.29445 (^c)</td>
<td>4.2714</td>
</tr>
<tr>
<td>MgS</td>
<td>5.135 (^d)</td>
<td>5.210</td>
</tr>
<tr>
<td>MgSe</td>
<td>5.406, (^e) 5.588, (^c) 5.420, (^d) 5.499 (^e)</td>
<td>5.463</td>
</tr>
<tr>
<td>CaO</td>
<td>4.871, (^c) 4.854, (^d) 4.750 (^e)</td>
<td>4.796</td>
</tr>
<tr>
<td>CaSe</td>
<td>6.103, (^c) 5.903, (^c) 6.003 (^e)</td>
<td>5.920</td>
</tr>
<tr>
<td>SrO</td>
<td>5.217, (^c) 5.055 (^e)</td>
<td>5.139</td>
</tr>
<tr>
<td>SrSe</td>
<td>6.465, (^c) 6.244, (^c) 6.363 (^e)</td>
<td>6.232</td>
</tr>
<tr>
<td>BaO</td>
<td>5.646, (^c) 5.465 (^e)</td>
<td>5.355</td>
</tr>
<tr>
<td>BaSe</td>
<td>6.78, (^f) 6.40 (^g)</td>
<td>6.600</td>
</tr>
<tr>
<td>BaTe</td>
<td>6.60, (^e) 6.06, (^b) 6.52, (^f) 6.86 (^g)</td>
<td>6.820</td>
</tr>
</tbody>
</table>

Results were calculated using: \(^a\) LDA (local density approximation); \(^b\) GGA (generalized gradient approximation); \(^c\) HF (Hartree-Fock); \(^d\) HF-PW (Hartree-Fock Perdew-Wang); \(^e\) HF-PZ (Hartree-Fock Perdew-Zunger); \(^f\) LAPW-LDA (linearized augmented plane-wave local density approximation); \(^g\) ASW-LDA (augmented spherical wave local density approximation).

### TABLE 1.2 Calculated bulk modulus (GPa) of alkaline earth chalcogenides with the B1 structure.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Theoretical Results</th>
<th>Experimental Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>185.9, (^a) 169.1, (^d) 186, (^c) 182 (^e)</td>
<td>156, 162</td>
</tr>
<tr>
<td>MgSe</td>
<td>777 (^a) (^g)</td>
<td></td>
</tr>
<tr>
<td>MgTe</td>
<td>627 (^a) (^g)</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>111, (^a) 120, (^c) 135 (^d)</td>
<td>111.2, 112.0</td>
</tr>
<tr>
<td>SrO</td>
<td>35.5, (^c) 32.3 (^d)</td>
<td>34.3</td>
</tr>
<tr>
<td>BaO</td>
<td>45.0, (^c) 40.8 (^d)</td>
<td>66.2</td>
</tr>
<tr>
<td>BaS</td>
<td>524, (^e) 524 (^g)</td>
<td>55.1, 394.2 (^g)</td>
</tr>
<tr>
<td>BaSe</td>
<td>468, (^a) 468 (^a) (^g)</td>
<td>400, 408–460 (^g)</td>
</tr>
<tr>
<td>BaTe</td>
<td>374.3, (^e) 374.3 (^g)</td>
<td>294 (^g)</td>
</tr>
</tbody>
</table>

\(^a\), \(^b\), \(^c\), \(^d\), \(^e\), \(^f\) Same as the remarks in TABLE 1.1; \(^g\) The unit is kbar.
### TABLE 1.3 The transition pressure (GPa) for alkaline earth chalcogenides.

<table>
<thead>
<tr>
<th>Name</th>
<th>Theoretical Results</th>
<th>Experimental Results</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>515, 220, 711.6, 515</td>
<td>&gt;100</td>
<td>B1-B2</td>
</tr>
<tr>
<td>MgTe</td>
<td>190.8</td>
<td>1-3.5</td>
<td>B4-B8</td>
</tr>
<tr>
<td>CaO</td>
<td>68.1, 75.1, 63.4, 66.3</td>
<td>60.0, 65.0</td>
<td>B1-B2</td>
</tr>
<tr>
<td>SrO</td>
<td>29.2, 42.3</td>
<td>36</td>
<td>B1-B2</td>
</tr>
<tr>
<td>BaO</td>
<td>17.4, 27.3</td>
<td>9, 14.5</td>
<td>B1-B2</td>
</tr>
<tr>
<td>BaS</td>
<td>60.25</td>
<td>65</td>
<td>B1-B2</td>
</tr>
<tr>
<td>BaSe</td>
<td>56, 60</td>
<td>60</td>
<td>B1-B2</td>
</tr>
<tr>
<td>BaTe</td>
<td>22.8, 45.27, 39.5</td>
<td>48</td>
<td>B1-B2</td>
</tr>
</tbody>
</table>

- Same as the remarks in TABLE 1.1; 1 PP-LCAO (pseudopotential linear combination of atomic orbitals); 2 B1, NaCl-type structure, \( F_{\text{mmm}} \), 225; 2 B2, CsCl-type structure, \( P_{\text{mmm}} \), 221; 3 B4: wurtzite structure, \( P_{\text{b}3\text{mc}} \), 186; 4 B8, NiAs-type structure, \( P_{01/\text{mmc}} \), 194; 5 The unit is kbar.

Also indicated from TABLES 1.1-1.3 that for alkaline earth chalcogenides, the theoretical results obtained using the GGA method are in agreement with experiments much better than the results calculated using other methods.

### 1.1.2 Band Structure, Density of State, and Energy Gap

Band structures and DOS are useful properties in understanding the electronic behaviors of materials, especially the semiconductors. Meanwhile, it is easy to calculate the theoretical results of these properties from a first-principles calculation. As a result, intensive theoretical researches have been launched for alkaline earth chalcogenides and many papers have been published in the literatures. Taking an example of BaTe, its band structure and DOS with the structure of B1 (NaCl type, \( F_{\text{mmm}} \), 225) or B2 (CsCl type, \( P_{\text{mmm}} \), 221) has been calculated using various methods.
such as LMTO (linear muffin-tin orbital), LDA, GGA, LAPW (linearized augmented plane-wave), and ASW (augmented spherical wave). Generally, in these works, comparisons were usually conducted between the theoretical results from different first-principles methods. For example, in Ref. 34, HF (Hartee-Fock) and LDA were used to study the band structures and DOS of MgO, CaO, SrO, MgS, CaS, and SrS. Sometimes, the comparisons were conducted between the theoretical results for a compound with different crystal structures. For example, in Ref. 35, the band structures and DOS of MgS and MgSe with a structure of B1 or B3 (Zinc-Blende structure, space group of 216) were calculated and discussed.

The energy gap also has been intensely studied using first-principles calculations. Again, the alkaline earth chalcogenides are ideal candidates for comparing the efficiency of different computational methods. For instance, in Ref. 36, the energy gaps of BeSe, BeTe, MgSe, and MgTe were obtained using the EXX (Exact-Exchange), GW-EXX (G represents the Green’s function and W represents the screened coulomb interaction.), LDA and GW-LDA methods. The results showed that GW method could achieve more accurate results, but a much more rigorous formalism was necessary. Another application of the energy-gap calculation is to investigate the metallization transition and predict the metallization pressure, which is discussed in last section. More detailed introductions can be found in Ref. 37.

1.1.3 Elastic Constant

The elastic constants of MgO, CaO, SrO, BaO, MgSe, CaSe, and SrSe were calculated using FP-LMTO-GGA (full-potential linear muffin-tin orbital granulized gradient approximation), HF, HF-PZ (Hartee-Fock Perdew-Wang) or HF-
PW (Hartee-Fock Perdew-Zunger). Theoretical details are described as follows.\textsuperscript{23}

The elastic constants of a crystal are defined as the second derivatives of the total energy density with respect to an infinitesimal strain tensor $\varepsilon$. In a cubic crystal structure, the strain

\[
\varepsilon = \begin{pmatrix}
\delta & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
\]

is adopted to each volume $V$ for calculating $C_{11}$ as

\[
C_{11} = \frac{1}{V} \frac{\partial^2 E}{\partial \delta^2} \bigg|_{\delta=0},
\]

where the $\delta$ is relative change in length. The $\varepsilon$ matrix for the calculation of $C_{44}$ is

\[
\varepsilon = \begin{pmatrix}
0 & \delta & \delta \\
\delta & 0 & \delta \\
\delta & \delta & 0 \\
\end{pmatrix}.
\]

Then, $C_{44}$ can be expressed as

\[
C_{44} = \frac{1}{12V} \frac{\partial^2 E}{\partial \delta^2} \bigg|_{\delta=0}.
\]

The $\varepsilon$ matrix for the calculation of $C_{11} - C_{12}$ is

\[
\varepsilon = \begin{pmatrix}
\delta & 0 & 0 \\
0 & -\delta & 0 \\
0 & 0 & 0 \\
\end{pmatrix}.
\]

Then,

\[
C_{11} - C_{12} = \frac{1}{2V} \frac{\partial^2 E}{\partial \delta^2} \bigg|_{\delta=0}.
\]
and

\[ C_{12} = C_{11} - (C_{11} - C_{12}) \]  \hspace{1cm} (1.14)

Here, \( C_{11}, C_{12}, \) and \( C_{44} \) are the three components of the elastic constant tensor. After getting \( E(\delta) \) under different \( \delta \) and fitting the total energies to obtain the second energy derivative, the elastic constants of \( C_{11}, C_{12}, \) and \( C_{44} \) can be derived.

Because there are no sufficient experimental results found in the literatures for alkaline earth chalcogenides, theoretical works in elastic-constant calculations have not draw much attention and only a few results can be found so far.\(^{23,38}\)

### 1.1.4 Charge Density

The charge-density calculations can be performed to get the information about the distributions of electrons in alkaline earth chalcogenides. These results are necessary to determine the characters of chemical bonds between elements. For example, in Ref. 39, the charge densities of MgO, CaO, and SrO indicated that the chemical bonds between the oxygen and metallic elements changed from ionic bonds in MgO to covalent bonds in SrO.

### 1.1.5 Cohesive Energy

In solid state physics, cohesive energy is defined as the energy that must be added to a crystal to separate its components as neutral free atoms with the same electronic configurations. Some summaries of the cohesive-energy calculations can be found in Refs. 22 and 40-42.
Usually, during a first-principles calculation, the cohesive energy of a crystal can be expressed as

\[ E_{co} = E_{tot} - E_{spin-pola} \]  \hspace{1cm} (1.15)

where, \( E_{co} \) is calculated cohesive energy, \( E_{tot} \) is the total energy and \( E_{spin-pola} \) is the total energy with spin-polarization effects included. Although cohesive energies have been successfully calculated using first-principles calculations for many compounds, no work on alkaline earth chalcogenides was reported due to insufficient experimental results. Thakur was the only one who calculated the cohesive energies of BeO, MgO, CaO, SrO, and BaO using three assumed interaction potential functions. However, he did not use any first-principles calculations in his work.

In brief, most of the theoretical calculations for alkaline earth chalcogenides have been focused on the pressure-induced phase transition or metallization, and some on the band structure, DOS, energy gap, and elastic constant. However, only a few works were reported to calculate the cohesive energy. No works were reported to calculate the Debye temperature and thermal expansion coefficient. Moreover, it seems that previous theoretical and experimental studies overlooked the fact that II-VI compounds can be good candidates for wide-band-gap semiconductors. II-VI compounds were intensively investigated as excellent candidates for wide-band-gap semiconductors only after 1991 when the blue-green-emitting semiconductors using ZnSe were first presented by Haase et al. Nevertheless, only a few works can be found to study the properties of barium chalcogenides and no attempt was made to study the effect of chemical bonds on the electronic properties of barium chalcogenides, which would be the objective of the present study.
1.2 Research Objectives

Most of II-VI compounds are wide-band-gap semiconductors and have been developed very quickly since the discovery of ZnSe by Haase et al. in 1991. However, the development of II-VI semiconductors is still a challenging task. For example, although ZnO has been investigated for many years as an excellent wide-band-gap semiconductor, it is very difficult to produce p-type ZnO because of a strong self-compensation effect arising from the presence of native defects or hydrogen impurities. As the increasing requirements for wide-band-gap semiconductors, this project was aimed to search new candidates for wide-band-gap semiconductors in barium chalcogenides. Firstly, the electronic properties of barium chalcogenides were systemically investigated using first-principles calculations. Secondly, the electronic behaviors in these materials were discussed and the relationships between the electronic properties and the chemical bonds are summarized from theoretical results. Finally, the behavior of the oxygen atom on the BaTe(111) surface was further investigated by first-principles calculations. Some suggestions are provided for experimental synthesis of new barium chalcogenides semiconductors.

1.3 Outline of the Thesis

In this chapter, the developed results from first-principles calculations in II-VI semiconductors are summarized. The objectives of this project are briefly addressed followed by an introduction of the thesis.

In the second chapter, theoretical background of density-functional theory is presented. Then, the commercial software for the first-principles calculations in this
In the third chapter, the structural and electronic properties of barium chalcogenides are systematically studied using first-principles calculations. The equilibrium lattice constants, density of states, charge densities, and energy gaps of all barium chalcogenides are calculated using both the GGA and LDA methods. Some theoretical results are compared with the experimental results. Further analyses are performed according to these theoretical results. Different electronic behaviors between the compounds with and without oxygen are observed. The possible reasons are discussed in terms of the characteristics of chemical bonds in barium chalcogenides.

In the fourth chapter, a possible experimental procedure to synthesize barium chalcogenides is first proposed. Then, the behavior of the oxygen atom on the BaTe(111) surface is studied using first-principles calculations. The theory for calculating surface energy from first-principles calculations is also introduced. After that, the supercells according to all possible configurations in the BaTe(111) surface, with and without defects, are prepared and their equilibrium structures are acquired using both the MD (molecular dynamics) and BFGS (Broyden-Fletcher-Goldfarb-Shano) optimizations. After compulsory convergence tests, the total energy of each optimized supercell is calculated before final surface-energy calculations. Finally, some discussions are given based on the calculated surface energies.

In the last chapter, the conclusions are given with some suggestions for future works.
Chapter 2: Density-Functional Theory and Computational Software

In this chapter, some background of density-functional theory (DFT) as well as the software I used for my project is introduced.

2.1 Introduction of Density-Functional Theory

Since the 1920’s, the theories behind quantum mechanics have been developed very quickly. It includes the findings and explanations of blackbody radiation and photoelectric effect in 1900’s. In 1913, Bohr proposed the model of hydrogen atom. Then, in 1923-1924, de Broglie made his great hypotheses, de Broglie’s Hypotheses. After that, in 1926, Schrödinger proposed the famous wave equation by which the description of electrons in a system became possible. Almost at the same time, the first-principles calculation was developed. Thomas (1926) and Fermi (1928) introduced the idea of expressing the total energy of a system as a functional of the total electron density. In 1960's, an exact theoretical framework called DFT was formulated by Hohenberg & Kohn (1964) and Kohn & Sham (1965), which provided the foundation for theoretical calculations. DFT is one of the most important methods in first-principles calculations. First-principles calculation means “start from the beginning”, which denotes that the theoretical calculation can be performed only with the information of elements and their positions in a system. In some references, it is also expressed as ab initio. In this section, some basic theories in DFT will be
introduced. For conciseness, all equations within are written in atomic units and the results are summarized according to Ref. 46.

### 2.1.1 Born-Oppenheimer Approximation

The Schrödinger equation for a system containing \( n \) electrons and \( N \) nuclei has the form of an eigenvalue problem,

\[
\hat{H}\Psi(r_1, \cdots, r_n, R_1, \cdots, R_N) = E\Psi(r_1, \cdots, r_n, R_1, \cdots, R_N),
\]

where \( \Psi \) is wave function, \( E \) is the total energy in the system, \( r_i \) and \( R_i \) are the coordinates of the \( i \)th electron and nucleus, respectively. Both \( r \) and \( R \) are vector variables. \( \hat{H} \) is the many-body Hamiltonian operator, given by

\[
\hat{H} = -\frac{1}{2} \sum_{\alpha} \frac{1}{m_\alpha} \nabla_\alpha^2 - \frac{1}{2} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \sum_i \sum_{j > i} \frac{1}{r_{ij}} - \sum_i \sum_{\alpha} \frac{Z_\alpha}{r_{ia}},
\]

where \( \nabla^2 \) is Laplacian operator, \( m_\alpha \) is the mass of nucleus \( \alpha \). The first term in Eq. 2.2 is the operator for the kinetic energy of the nuclei \( \alpha \). The second term is the operator for the kinetic energy of the \( i \)th electron. The third term is the potential energy of the repulsion between the nuclei, and \( R_{\alpha\beta} \) being the distance between nuclei \( \alpha \) and \( \beta \) with atomic numbers \( Z_\alpha \) and \( Z_\beta \). The fourth term is the potential energy of the repulsion between the electrons, and \( r_{ij} \) being the distance between electrons \( i \) and \( j \). The last term is the potential energy of the attraction between electrons and nuclei, and \( r_{ia} \) being the distance between electron \( i \) and nucleus \( \alpha \).

The Born-Oppenheimer approximation is based on the fact that the mass of the ions is much larger than that of the electrons. This implies that the typical electronic velocities are much larger than the ionic ones, and consequently, the degrees of
freedom of the electrons and the ions can be uncoupled. In other words, the electrons can be assumed to be practically always in their instantaneous ground states. The total wave function is therefore written as the product of the nuclear and electronic parts:

\[ \Psi(r_1, \cdots, r_n, R_1, \cdots, R_N) = \Psi_{el}^{(1)}(r_1, \cdots, r_n) \Psi^{(1)}(R_1, \cdots, R_N), \]

where \( \Psi(R_1, \cdots, R_N) \) is the wave function of nucleus and \( \Psi_{el}^{(1)}(r_1, \cdots, r_n) \) is the electronic wave function which is nucleus position dependent.

Finally, the Schrödinger equation can be separated into two parts: the time-independent Schrödinger equation of electrons in the constant field of the fixed nuclei, and the time-dependent Newton-like equation of movement for nuclei. A further approximation is to treat the nuclei like classical particles, so that the nuclear position operators can all be turned into position variables. The quantum effects are then limited to the electronic wave functions, which obey a simple Schrödinger equation

\[ \hat{H}^{el} \Psi_{el}^{(1)}(r_1, \cdots, r_n) = E_{el}^{(1)} \Psi_{el}^{(1)}(r_1, \cdots, r_n) \]

with

\[ \hat{H}^{el} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i,j=1}^{n} \frac{1}{r_{ij}} - \sum_i \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i,j=1}^{n} \frac{1}{r_{ij}} + \sum_i v_{ext}(r_i), \]

where \( v_{ext}(r_i) \) is the potential energy of the \( i \)th electron in the field of all nuclei.

The Born-Oppenheimer approximation is the first of several approximations made when trying to solve Schrödinger equations in complex systems rather than the system with only one or two electrons. In brief, it separates electron and nuclear motion based on the idea that nuclear mass is much larger than electron mass that the nuclei are basically "fixed" particles. The approximation removes the extremely difficult
problem of calculating the interactions between moving electrons and ions and, consequently, makes it possible to apply the Schrödinger equation to complex systems.

2.1.2 Hohenberg-Kohn Theorem and Variational Theorem

2.1.2.1 Hohenberg-Kohn Theorem

Density-functional theory is essentially based on two theorems presented by Hohenberg and Kohn. The first one is\textsuperscript{46}

For a system of $n$ interacting electrons, the all electrons’ many-body ground-state wave function $\Psi(r_1,\ldots,r_n)$ is a unique functional of the electronic density $\rho(r)$.

Here, $\rho(r)$ is the electron density and defined by

$$\rho(r) = n\int_0^\infty \int_0^\infty \ldots \int_0^\infty |\Psi(r_1,\ldots,r_n)|^2 \, dr_1 \cdots dr_n.$$  \tag{2.6}

It determines the probability of finding any of the $n$ electrons within the volume $dr$ (with arbitrary spin). Some of its fundamental properties are

$$\rho(r \to \infty) = 0 \quad \text{and} \quad \int \rho(r) dr = n,$$  \tag{2.7}

where, $r$ is the position vector of electron in system. The immediate result of this theorem is that all physically measurable quantities based on the electronic structures are unique functions of the electronic ground-state density alone. Hohenberg and Kohn proved the theorem for molecules with a nondegenerate ground state in 1964.\textsuperscript{47}

The pure electronic Hamiltonian is the sum of electronic kinetic-energy terms, electron-nuclear attractions, and electron-electron repulsions. Take the average for the
ground state, we have \( E = \bar{T} + \bar{V}_{Ne} + \bar{V}_{ee} \), where over bars denote averages, \( T \) is the kinetic energy in the studied system, \( V_{Ne} \) is the potential energy between nuclei and electrons and \( V_{ee} \) is the potential energy between electrons, respectively. Each of the average valuables in this equation is a molecular property determined by the ground-state electronic wave function \( \rho_0(r) \). Therefore, the total energy is

\[
E_0 = E_v[\rho_0] = \bar{T}[\rho_0] + \bar{V}_{Ne}[\rho_0] + \bar{V}_{ee}[\rho_0].
\]

From Eq. 2.5, the potential energy between electrons and nuclei is expressed as

\[
\bar{V}_{Ne} = \sum_{i=1}^{n} \nu(r_i) = -\sum_{i=1}^{n} \sum_{a} \frac{Z_a}{r_{ia}}. \]

Hence,

\[
\bar{V}_{Ne} = \left\langle \rho_0 \sum_{i=1}^{n} \nu(r_i) \psi_0 \right\rangle = \int \rho_0(r) \nu(r) \, dr,
\]

where \( \nu(r) \) is the nuclear attraction potential-energy function for an electron located at point \( r \). Hence, \( E_0 \) (Hohenberg-Kohn equation) can be expressed as follows:

\[
E_0 = E_v[\rho_0] = \bar{T}[\rho_0] + \bar{V}_{Ne}[\rho_0] + \int \rho_0(r) \nu(r) \, dr.
\]

### 2.1.2.2 Hohenberg-Kohn Variational Theorem

The second Hohenberg-Kohn theorem is essentially a minimum principle for the density. In contrast to the ordinary variational principle, which is formulated only with respect to the wave functions in combination with the energy functional, it states that

\[
\text{For every trial density function } \rho_n(r) \text{ that satisfies } \int \rho_n(r) \, dr = n \text{ and } \rho_n(r) \geq 0 \text{ for all } r, \text{ the following inequality holds: } E_0[\rho_0(r)] \leq E_v[\rho_n(r)], \text{ where } E_0 \text{ and } E_v \text{ are the energy functional in Section 2.1.2.1. In other words, the true ground-state electron density minimizes the energy functional } E_v[\rho_n(r)].
\]
Now suppose $\rho_{tr}$ as a trial density function. From the first Hohenberg-Kohn theorem, $\rho_{tr}$ determines the external potential $\nu_{tr}$ and this in turn determines the wave function $\psi_{tr}$ which is corresponding to the density $\rho_{tr}$. The variation theorem gives

$$E_{\psi} [\rho_{tr}] = E_{\psi} \geq E_0 = E_{\psi} [\rho_0],$$  \hspace{1cm} 2.11

with

$$E_{\psi} [\rho_{tr}] = \langle \psi_{tr} | \hat{H} | \psi_{tr} \rangle = \langle \psi_{tr} | \hat{T} + \hat{V}_{\nu} + \sum_{i=1}^{Z} \nu(r_i) | \psi_{tr} \rangle = \hat{T}[\rho_{tr}] + \hat{V}_{\nu}[\rho_{tr}] + \int \rho_{tr}(r) \nu(r) dr .$$  \hspace{1cm} 2.12

It means that any trial electron density cannot give a ground-state energy smaller than that of the true ground-state system. The minimum value of the total energy functional is the ground-state energy of the system.

### 2.1.3 Kohn-Sham Method

The Hohenberg-Sham theorem shows that it is possible in principle to calculate all ground-state molecular properties from $\rho_0$, without having to find the molecular wave function. The remaining problem is how to calculate $E_0$ from $\rho_0$ and how to find $\rho_0$ without first finding the wave function. In 1965, Kohn and Sham devised a practical method for finding $\rho_0$ and $E_0$.\(^{48}\)

In terms of wave function, the total electronic energy for many-body system is given by Hohenberg-Kohn equation:

$$E_{\psi} [\rho] = \hat{T}[\rho] + \hat{V}_{\nu}[\rho] + \int \rho(r) \nu(r) dr .$$  \hspace{1cm} 2.13

There are no closed expressions to calculate the first two parts. In order to turn DFT into a practical tool for real calculations, Kohn and Sham introduced a fictitious
reference system (denoted by the subscript \( s \)) of non-interacting electrons that each electron experiences the same external potential-energy function \( \nu_s(r_i) \), where \( \nu_s(r_i) \) is such as to make the ground-state electron density \( \rho_s(r) \) of the reference system equal to the exact ground-state electron density \( \rho_0(r) \) of the molecule studied, i.e., \( \rho_s(r) = \rho_0(r) \). So the Hamiltonian operator of the reference system is

\[
\hat{H} = \sum_{i=1}^{n} \left[ \frac{-1}{2} \nabla_{i}^{2} + \nu_{s}(r_{i}) \right] = \sum_{i=1}^{n} \hat{h}_{i}^{KS},
\]

where superscript \( KS \) denotes Kohn-Sham, \( \hat{h}_{i}^{KS} = \frac{-1}{2} \nabla_{i}^{2} + \nu_{s}(r_{i}) \) and \( \hat{h}_{i}^{KS} \) is the one-electron Kohn-Sham Hamiltonian operator. As a result, the single-particle wave function of the independent electron gas will be an eigenfunction of the operator \( \hat{h}_{i}^{KS} \):

\[
\hat{h}_{i}^{KS} \varphi_{i}^{KS} = \varepsilon_{i}^{KS} \varphi_{i}^{KS},
\]

where \( \varepsilon_{i}^{KS} \) is Kohn-Sham orbital energy.

Now define the electron density as

\[
\rho = \sum_{i} \left| \varphi_{i}^{KS} \right|^2.
\]

Then, let \( \Delta \overline{\rho} \) be the difference between the average ground-state-electron kinetic energy among the molecules and the reference system of non-interacting electrons with electron density equal to that in the molecule,

\[
\Delta \overline{\rho} = \rho \overline{\rho} - \overline{\rho},
\]

and

\[
\Delta V_{ee} = \rho(r) \rho(r) \frac{1}{2} \int d{r_1} d{r_2} ,
\]

\[
\Delta \overline{\rho} = \rho \overline{\rho} - \overline{\rho},
\]

\[
\Delta V_{ee} = \rho(r) \rho(r) \frac{1}{2} \int d{r_1} d{r_2} ,
\]

\[
\Delta \overline{\rho} = \rho \overline{\rho} - \overline{\rho},
\]

\[
\Delta V_{ee} = \rho(r) \rho(r) \frac{1}{2} \int d{r_1} d{r_2} ,
\]

\[
\Delta \overline{\rho} = \rho \overline{\rho} - \overline{\rho},
\]

\[
\Delta V_{ee} = \rho(r) \rho(r) \frac{1}{2} \int d{r_1} d{r_2} ,
\]

\[
\Delta \overline{\rho} = \rho \overline{\rho} - \overline{\rho},
\]

\[
\Delta V_{ee} = \rho(r) \rho(r) \frac{1}{2} \int d{r_1} d{r_2} ,
\]
where $\overline{T}_s[\rho]$ is the kinetic energy of the reference system of non-interacting electrons.

The second term in Eq. 2.18 is the classical expression of the electrostatic repulsion energy if the electrons are smeared out into a continuous distribution of charge with electron density $\rho$. With the definitions, rewrite the Hohenberg-Kohn equation as

$$E_0[\rho] = \int \rho(r) \varphi(r) dr + \overline{T}_s[\rho] + \frac{1}{2} \iiint \frac{\rho(r_1) \rho(r_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\rho], \quad 2.19$$

where $E_{xc}[\rho]$ is the exchange-correlation energy functional. It is defined by

$$E_{xc}[\rho] = \Delta \overline{T}[\rho] + \Delta V_{xc}[\rho]. \quad 2.20$$

Minimize the energy to yield the Kohn-Sham equation, which reads like

$$\left[ -\frac{1}{2} \nabla^2 + \nu_H(r) + \nu_{xc}(r) + \nu_{co}(r) \right] \varphi_i(r) = \hat{H}^{KS} \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad 2.21$$

with

$$\nu_H(r) = \int \frac{\rho(r_2)}{r_{12}} d\mathbf{r}_2, \quad \nu_{xc}(r) = \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_\alpha|} \quad \text{and} \quad \nu_{co}(r) = \int \frac{\rho(r_2)}{r_{12}} d\mathbf{r}_2, \quad 2.22$$

where $\nu_H$ is Hartree potential energy. The exchange-correlation energy $E_{xc}$ contains the following components: the kinetic correlation energy $\Delta \overline{T}$, the exchange energy (which arises from the antisymmetry requirement), the Coulombic correlation energy (which is associated with inter-electronic repulsions) and a self-interaction correction.

2.1.4 Local Density Approximation and Generalized Gradient Approximation

To proceed with a practical calculation, the difficulty is how to reformulate the exchange-correlation energy functional. An approximation has to be made for this expression and the most famous one is the local density approximation (LDA) which
yields good results in a large number of systems and is still used for first-principles calculations.

In the LDA formalism, the functional for the exchange-correlation energy is chosen to have the same formal expression as the one of a uniform electron gas:

$$E^{\text{LDA}}_{\text{xc}}(\rho) = \int \rho(r) \varepsilon^{\text{LDA}}_{\text{xc}}(\rho) \, dr ,$$  \hspace{1cm} 2.23

where $\varepsilon^{\text{LDA}}_{\text{xc}}$ is the exchange-correlation energy per particle of the uniform electron gas. It’s well known that LDA often underestimates the theoretical results such as equilibrium volume and energy gap. An obvious approximation for improving the LDA results is to include the gradient corrections, by making the functional of the density and its gradient $|\nabla \rho|$. It is called as the generalized gradient approximation (GGA).\textsuperscript{49} The exchange-correlation energy in the GGA method has a form of

$$E^{\text{GGA}}_{\text{xc}}(\rho) = \int \rho(r) \varepsilon^{\text{GGA}}_{\text{xc}}(\rho, |\nabla \rho|) \, dr ,$$  \hspace{1cm} 2.24

where $\varepsilon^{\text{GGA}}_{\text{xc}}$ is the exchange-correlation energy per particle of the uniform electron gas with the gradient of density considered.

### 2.2 Introduction of Computational Software

All theoretical calculations in this project are performed using CASTEP (the Cambridge Serial Total Energy Package). CASTEP was first developed by Payne in 1986.\textsuperscript{50} Later, more and more authors added many features into this code such as gradient-corrected function and ultrasoft pseudopotentials. Now, CASTEP is one of the software packages in Cerius\textsuperscript{2} which is distributed by Accelrys. As one of the famous softwares to make DFT practicable, CASTEP has been applied by many
researchers into different systems such as bulk materials, surfaces, liquids, organics, and inorganics. It is also the principle tool in our calculations and hence, some important technological characters in CASTEP\textsuperscript{51} are introduced in this section.

### 2.2.1 Plane Waves

In CASTEP, plane waves are employed for the expansion of each single-electron wave function \( \psi(r) \), that is

\[
\psi(r) = \sum_i u(G) \exp(i(k + G) \cdot r).
\]

The \( u(G) \) is the expansion coefficient, \( k \) is the wave vector in the first Brillouin zone (BZ). The wave vectors \( G \) are such that the plane waves are commensurate with the supercell. The number of plane waves included in the expansion is limited by the kinetic cutoff energy.

The advantages for the plane-wave basis set are

- It is unbiased, so that all space is treated the same.
- It is complete.
- There is a single convergence criterion.
- Plane waves are mathematically simple.
- Plane waves do not depend on atomic positions.

There are some disadvantages too.

- The number of plane waves needed is determined by the greatest curvature of the wave function.
- Empty space has the same quality of representation and cost as regions of interest.
2.2.2 Pseudopotential

The basic idea of pseudopotential is to replace the real potential in a system, arising from the nuclear charges and the core electrons, with an effective potential inside and outside a core region. These pseudo-electrons experience exactly the same potential outside the core region as the original electrons but have a much weaker potential inside the core region. It makes the solution of the Schrödinger equation much simpler by allowing the expansion of the wave function into a relatively small set of plane waves. Certain demands are placed on this effective potential. Firstly, it must be such that the valence orbital eigenvalues are the same as those in an all-electron calculation on the atom. Secondly, it must also preserve the continuity of the wave functions and their first derivatives across the core boundary. Finally, integrating the charge in the core region should give the same answer for the pseudo-atom and the all-electron one.

In CASTEP, a much more transferable one, the ultrasoft pseudopotential which was developed by Vanderbilt, is provided.

2.2.3 k-Point Sampling

For a periodic system, integrals in real space over infinitely extended system can be replaced by integrals over the finite first BZ in reciprocal space according to Bloch's theorem. Usually, such integrals are performed by summing the function values of the integrand (for instance, the charge density) at finite points in the first BZ, called k-point mesh. CASTEP offers one method to choose special k points according to the scheme proposed by Monkhorst and Pack. In the scheme, the k points are distributed homogeneously in the BZ, with rows or columns of k points running parallel to the reciprocal lattice vectors that span the BZ.
Because the plane-wave basis and pseudopotential approximations are conducted in CASTEP, the theoretical calculations using CASTEP are also regarded as the plane-wave pseudopotential (PWP) calculation in some research works.
Chapter 3: Calculated Structural and Electronic Properties of Bulk Barium Chalcogenides

In this chapter, the structural and electronic properties of all barium chalcogenides in crystal structure were systematically studied using CASTEP. The group VI elements experience a change from a typical nonmetal of oxygen to a metal of polonium with increasing atomic number. Consequently, the chemical bonds between barium and chalcogens change from ionic to metallic bonds. The different chemical bonds in barium chalcogenides would influence the properties of the compounds, especially the electronic properties. In this chapter, the relationship between the electronic properties and the chemical bonds in barium chalcogenides was investigated. Our conclusions are expected to be helpful in the design of new wide-band-gap II-VI semiconductors.

3.1 Structural Properties in Barium Chalcogenides

The properties, such as the equilibrium lattice constants (LCs), band structures, densities of state and energy gaps of all binaries, i.e., BaO, BaS, BaSe, BaTe, and BaPo, were calculated based on both the GGA and LDA methods from first-principles calculations. Then, the body-center group VI atoms in certain binaries were substituted by another kind of the group VI atoms, which changed the space group of the compounds from 225 (B1 structure, NaCl type, $F_{\text{m}}$m) to 221 (B2 structure, CsCl...
For instance, when a tellurium atom substituted the body-center oxygen atom in BaO, a new compound with a formula of BaTe$_{0.25}$O$_{0.75}$ was obtained. In this compound, some Ba–O chemical bonds in BaO were replaced by Ba–Te chemical bonds, as shown in Fig 3.1. The properties of all new compounds were obtained with the help of the first-principles calculations. From the theoretical results, correlations between the properties and the chemical bonds in barium chalcogenides were established. All artificial compounds and their substitutions are listed in TABLE 3.1.

### 3.1.1 Lattice Constants of Barium Chalcogenides

Usually, in any first-principles calculation, the total energies at various LCs must be obtained for calculating equilibrium LC. In this study, the total energies of barium chalcogenides at different volumes were calculated using both the GGA and LDA methods. After that, calculated total energies were fitted by the third-order Birch-Murnaghan’s equation of state using least-squares method and obtained equilibrium volume $V_0$, bulk modulus $B$, and its pressure derivative $B'$. The third-order Birch-Murnaghan’s equation of state is given as Eq. 1.5 in Chapter one.

In Figs. 3.2 and 3.3, the curves of total energies at various LCs are shown. For accuracy, two steps were used when searching for the equilibrium LC of a compound. First, the total energies were calculated with a large interval of LC between two continuous calculations. We used 0.1 Å in our calculations. The LC corresponding to the minimum of total energy was regarded as a reference equilibrium LC. Second, a more rigorous calculation was carried out near the former reference equilibrium LC with a smaller interval of LC (0.05 Å here), a larger cutoff energy and k points. The LC corresponding to the minimum of total energy at this time was the theoretical
FIG. 3.1 Substitution of the body-center oxygen atom in (a) BaO by a tellurium atom to obtain (b) BaTe_{0.25}O_{0.75}. The black, white, and grey balls represent barium, oxygen, and tellurium atoms, respectively.

<table>
<thead>
<tr>
<th>Name</th>
<th>Substitution Operator</th>
<th>Substitution Operator</th>
<th>Substitution Operator</th>
<th>Substitution Operator</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{BaS}<em>{0.75}\text{O}</em>{0.25} )</td>
<td>S in BaS by O</td>
<td>O in BaO by S</td>
<td>S in BaS by Se</td>
<td>Se in BaSe by S</td>
</tr>
<tr>
<td>( \text{BaS}<em>{0.25}\text{O}</em>{0.75} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{BaS}<em>{0.75}\text{Se}</em>{0.25} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{BaS}<em>{0.25}\text{Se}</em>{0.75} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.1 All studied ternary compounds.
FIG. 3.2 Calculated total energy (eV) using the GGA method vs lattice constant (Å) for all compounds. The equilibrium lattice constants are corresponding to the minimum of total energy.
FIG. 3.3 Calculated total energy (eV) using the LDA method vs lattice constant (Å) for all compounds. The equilibrium lattice constants are corresponding to the minimum of total energy.
equilibrium LC of the compound. Figs. 3.2 and 3.3 give the results of all compounds calculated using both the GGA and LDA methods. All results are also listed in Appendix A with the details of the computational parameters. In TABLE 3.2, calculated equilibrium LCs, bulk modulus, and their pressure derivation are presented.

From TABLE 3.2, it is obvious that the LDA method always underestimates the results of the studied compounds while the GGA method decreases this error. It coincides with the empirical experience found in other first-principles calculations. However, there are no reasons to declare that the GGA method can always get a better result than the LDA method, or the GGA method is better than the LDA method. It depends on which one coincides with experimental results better. GGA is better than LDA in our studied barium chalcogenides because, for all binaries, the LCs obtained using the GGA method match the experimental results better than those obtained using the LDA method. For ternaries, the calculated LCs are reasonable since, as we know, a substitution of the body-center atom by a larger one enlarges the LC, while by a smaller one decreases it. As a result, the theoretical LC of BaTe_{0.75}O_{0.25} is smaller than that of BaTe, whereas the theoretical LC of BaTe_{0.25}O_{0.75} is larger than that of BaO. All theoretical LCs in TABLE 3.2 are treated as the equilibrium volumes for proceeding with further calculations.

After the equilibrium LCs of all compounds were calculated using both the GGA and LDA methods, the electronic properties could be calculated based on the theoretical LCs. However, because of the limitation of modern computers, a convergence test was first necessary to determine the computational parameters first so that the accurate results could be calculated with the least time. The convergence tests for all
TABLE 3.2 Calculated and experimental\(^a\) equilibrium lattice constants (LCs, Å), bulk modulus B (kbar), and pressure derivative of the bulk modulus B’. The results are calculated by fitting Birch-Murnaghan’s equation of state.

<table>
<thead>
<tr>
<th></th>
<th>BaO</th>
<th>BaS</th>
<th>BaSe</th>
<th>BaTe</th>
<th>BaPo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GGA</td>
<td>LDA</td>
<td>Exp.</td>
<td>GGA</td>
<td>LDA</td>
</tr>
<tr>
<td>B</td>
<td>714</td>
<td>846.1</td>
<td>-</td>
<td>425.6</td>
<td>511.0</td>
</tr>
<tr>
<td>B’</td>
<td>4.70</td>
<td>3.50</td>
<td>-</td>
<td>4.50</td>
<td>4.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>BaTe</th>
<th>BaPo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GGA</td>
<td>LDA</td>
</tr>
<tr>
<td>LC</td>
<td>6.989</td>
<td>6.869</td>
</tr>
<tr>
<td>B</td>
<td>311.8</td>
<td>351.3</td>
</tr>
<tr>
<td>B’</td>
<td>7.60</td>
<td>4.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ba(<em>{0.25})(\text{Se}</em>{0.75})</th>
<th>Ba(<em>{0.75})(\text{O}</em>{0.25})</th>
<th>Ba(<em>{0.75})(\text{Se}</em>{0.25})</th>
<th>Ba(<em>{0.25})(\text{Se}</em>{0.75})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC(^b)</td>
<td>5.839</td>
<td>6.245</td>
<td>6.462</td>
<td>6.584</td>
</tr>
<tr>
<td>LC(^c)</td>
<td>5.720</td>
<td>6.126</td>
<td>6.328</td>
<td>6.427</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ba(<em>{0.75})(\text{Se}</em>{0.25})</th>
<th>Ba(<em>{0.25})(\text{Te}</em>{0.75})</th>
<th>Ba(<em>{0.25})(\text{O}</em>{0.75})</th>
<th>Ba(<em>{0.75})(\text{Te}</em>{0.25})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC(^b)</td>
<td>6.745</td>
<td>6.909</td>
<td>6.113</td>
<td>6.783</td>
</tr>
<tr>
<td>LC(^c)</td>
<td>6.585</td>
<td>6.777</td>
<td>5.988</td>
<td>6.650</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 9 and the references therein; \(^b\) Results from the GGA method; \(^c\) Results from the LDA method.
compounds in this work were performed using the GGA method. During the tests, the total energies at various cutoff energies were calculated with the number of k points for the BZ integration unchanged (10 k points). The results of convergence tests for all compounds are shown in Fig. 3.4.

The curves in Fig. 3.4 are plotted according to the total energies at various cutoff energies. It is clear from Fig. 3.4 that, with the increase of the cutoff energy during the convergence tests, the total energy of a system is stable at certain value. The larger the cutoff energy is used, the more the numbers of plane waves are applied for expanding the wave function of electrons and the better the coincidence between the theoretical total energy and the stable one in system is obtained, while much more computational time has to be spent in the calculations. Usually, in any first-principles calculation, a calculation with larger cutoff energies and k points can get more accurate results with the consumption of total computational time. How to find the balance between these factors is important for every first-principles calculation. Fig. 3.4 shows that a cutoff energy of 300 eV with 10 k points is enough to get the convergences of total energy at an acceptable computational time for all compounds. As a result, in the following calculations, a cutoff energy of 300 eV and 10 k points are employed.

### 3.1.2 Total Energies of Barium Chalcogenides

Before calculating the electronic properties of barium chalcogenides, it is required in CASTEP to do a single-point-energy calculation for each compound to obtain the wave functions for all electrons in the supercell. Currently, the single-point-energy calculation for each compound was performed first using both the GGA (GGA-PW91 code beyond the GGA functional, which was developed by Perdew and Wang\(^5\))
FIG. 3.4 Convergence tests for all compounds using the GGA method.
and LDA methods. The configurations of valence electrons in the calculations were
$5s^25p^66s^2$ for barium and $ns^2np^4$ for chalcogens ($n$ is the period number in the periodic
table of elements.). Meanwhile, the ultrasoft pseudopotential was employed to
simulate the potential energy outside the core electrons in each atom. For each
compound, a supercell with the structure of B1 (NaCl type, $F_{m\overline{3}m}, 225$) for binaries or
B2 (CsCl type, $P_{m\overline{3}m}, 221$) for ternaries was used for first-principles calculations and
in each supercell, there were eight atoms and 64 valence electrons. According to the
results from convergence tests, a cutoff energy of 300 eV and 10 special k points
corresponding to a $6\times6\times6$ Monkhorst-Park mesh were adopted for single-point-energy
calculations. All computational parameters are listed in TABLE 3.3.

### 3.2 Electronic Properties in Barium Chalcogenides

Band structure is one of the important properties for a semiconductor. The band
structures of all compounds in this work were calculated using both the GGA and
LDA methods. There are 64 valence electrons within 32 bands in each unit cell.
However, for calculating the energy gap, 36 bands with four unoccupied conduction
bands were calculated. The energy gap, which was defined as minimum gap between
the conduction and valence bands, were derived from the calculated band structure of
a compound. Meanwhile, as mentioned above, the chemical bonds in these
compounds are one of the important factors influencing the electronic properties and
they could be discussed according to the results of charge densities. Hence, the charge
densities of all compounds were also calculated to investigate the distributions of the
electrons in the compounds. In the meantime, the DOS of each compound was studied
to make a full understanding of the electronic properties in barium chalcogenides. All
<table>
<thead>
<tr>
<th>Name</th>
<th>Cutoff Energy in Single-Point-Energy &amp; Charge-Density Calculations*</th>
<th>Total Electrons in PDOS* and DOS* Calculations</th>
<th>Total Bands in Band-Structure Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaO</td>
<td>300 eV $\rightarrow$ 27$\times$27</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaS</td>
<td>300 eV $\rightarrow$ 32$\times$32</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaSe</td>
<td>300 eV $\rightarrow$ 32$\times$32</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaTe</td>
<td>300 eV $\rightarrow$ 36$\times$36</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaPo</td>
<td>300 eV $\rightarrow$ 36$\times$36</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaS$<em>{0.75}$O$</em>{0.25}$</td>
<td>300 eV $\rightarrow$ 30$\times$30</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaS$<em>{0.25}$O$</em>{0.75}$</td>
<td>300 eV $\rightarrow$ 30$\times$30</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaS$<em>{0.75}$Se$</em>{0.25}$</td>
<td>300 eV $\rightarrow$ 32$\times$32</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaS$<em>{0.25}$Se$</em>{0.75}$</td>
<td>300 eV $\rightarrow$ 32$\times$32</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaSe$<em>{0.75}$Te$</em>{0.25}$</td>
<td>300 eV $\rightarrow$ 36$\times$36</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaSe$<em>{0.25}$Te$</em>{0.75}$</td>
<td>300 eV $\rightarrow$ 36$\times$36</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaTe$<em>{0.75}$O$</em>{0.25}$</td>
<td>300 eV $\rightarrow$ 32$\times$32</td>
<td>128</td>
<td>36</td>
</tr>
<tr>
<td>BaTe$<em>{0.25}$O$</em>{0.75}$</td>
<td>300 eV $\rightarrow$ 30$\times$30</td>
<td>128</td>
<td>36</td>
</tr>
</tbody>
</table>

*a* Totally, 10 k points corresponding to 0.03 $\rightarrow$ 6$\times$6 Monkhorst-Park mesh for each compound; *b* Density of state; *c* Partial density of state.
computational parameters are also listed in TABLE 3.3.

All calculated band structures, DOS, and partial densities of state (PDOS) using the GGA method are shown in Figs. 3.5-3.7. Because the results from the GGA and LDA methods are similar, only the results using the GGA method are presented.

3.2.1 Band Structure

When calculating the band structures, special routes were chosen to run through some high-symmetry points in the first BZ, such as \( \Gamma \) (000), \( R \left( \frac{1}{2} \frac{1}{2} \frac{1}{2} \right) \), and \( \chi \left( \frac{1}{2} \frac{1}{2} 0 \right) \). The results of all compounds using the GGA method are shown in Fig. 3.5. It is shown that all compounds are direct band-gap semiconductors with the energy gap in the \( \Gamma \) point (The energy gap between the conduction and valence bands at the point is minimum. It is denoted as \( \Gamma-\Gamma \) thereinafter.). However, it is known from experimental results that all binaries are indirect band-gap semiconductors with the energy gaps between the \( \Gamma \) point in the valence bands and the \( \chi \) point in the conduction bands (denoted as \( \Gamma-\chi \) thereinafter).55,56 The conflict can be explained by the fact that, in CASTEP, a self-consistent-field (SCF) method is employed. During SCF method, a calculation is finished when the difference of the total energies between last two iterations is lower than the energy tolerance, a parameter set before the calculations. In this work, an energy tolerance of 0.00002 eV per atom is employed. In other words, the SCF calculation is only to minimize the total energy in supercell. According to Hohenberg-Kohn variational theorem, the wave functions for minimizing the total energy can only be regarded as one possible solution of the ground states for all electrons in the supercell. There are no reasons to conclude that the wave functions
FIG. 3.5 Calculated band structures for all compounds using the GGA method.
FIG. 3.6 Calculated densities of state (DOS) for all compounds using the GGA method.
FIG. 3.7 Calculated partial densities of state (PDOS) for all compounds using the GGA method.
from SCF are just as same as the expressions of the ground states in the original system. The issue can be proved by the results from an additional first-principles calculation. Band structures of binaries in Fig. 3.5 are calculated using a unit cell of face-centered-cubic (FCC) structure. Their band structure was recalculated using a primitive cell of FCC structure. The results are presented in Fig. 3.8. It is interesting to find that, except for BaO, all binaries are indirect band-gap semiconductors with the energy gap of Γ-X. For BaO, although it is direct band-gap semiconductor, the energy gap comes from X-X, in contrast to Γ-Γ in the unit-cell calculation. The results imply that, without the help of experimental data, it is difficult to predict the type of a semiconductor only from the calculated band structure. However, although we cannot determine the type of a semiconductor from theoretical band structures, the energy gaps calculated using either primitive cell or unit cell seem to be equal to each other. All energy gaps (calculated using either primitive cells or unit cells while with the GGA or LDA method. Some experimental data of binaries are also listed.) are presented in TABLE 3.4. For a comprehensive comparison, all theoretical gaps of Γ-Γ, Γ-X, and X-X calculated with both the GGA and LDA methods are also listed in TABLE 3.4. It is clear that the calculated energy gaps using unit cells (Γ-Γ) are the same as the results using primitive cells (Γ-X while X-X for BaO) except BaSe. For BaSe, its energy gap is only 0.01 eV lower than the one using the primitive-cell calculation. We proceeded with the unit-cell calculations for all binaries because the unit cell of a $F_{m\overline{3}m}$ structure in binary was similar to the primitive cell of $P_{m\overline{3}m}$ in ternary. As a result, all calculated theoretical electronic properties between binaries and ternaries were comparable. TABLE 3.4 also indicates that, for binaries, all theoretical energy gaps using the GGA and LDA methods are smaller than the experimental results, while the LDA method underestimates the results greater than
FIG. 3.8 Calculated band structures using primitive cells. The results were calculated using the GGA method. A cutoff energy of 400 eV and 10 special k points were employed in the calculations. The coordinates for special high-symmetry points in the first BZ are \( X \left( \frac{1}{2}, 0, 0 \right) \), \( W \left( \frac{1}{2}, \frac{1}{4}, 0 \right) \), \( K \left( \frac{3}{8}, \frac{3}{8}, 0 \right) \), \( \Gamma \) (000), and \( L \left( \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \right) \). All calculated energy gaps are also listed in TABLE 3.4.
TABLE 3.4 Calculated energy gaps of Γ-Γ, Γ-X, and X-X using primitive cells. Calculated energy gaps using unit cells and the experimental results of binaries are also listed for comparison.

<table>
<thead>
<tr>
<th>Compound</th>
<th>GGA $\Gamma$-Γ</th>
<th>GGA $\Gamma$-X</th>
<th>GGA X-X</th>
<th>LDA $\Gamma$-Γ</th>
<th>LDA $\Gamma$-X</th>
<th>LDA X-X</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaO</td>
<td>2.09</td>
<td>3.08</td>
<td>3.28</td>
<td>2.09</td>
<td>1.67</td>
<td>2.73</td>
<td>2.99 4.10, 3.88^d</td>
</tr>
<tr>
<td>BaS</td>
<td>2.17</td>
<td>2.85</td>
<td>3.02</td>
<td>2.17</td>
<td>1.83</td>
<td>2.57</td>
<td>2.73 3.90, 3.88^d</td>
</tr>
<tr>
<td>BaSe</td>
<td>2.02</td>
<td>2.64</td>
<td>2.86</td>
<td>2.01</td>
<td>1.63</td>
<td>2.31</td>
<td>2.54 3.60, 3.58^d</td>
</tr>
<tr>
<td>BaTe</td>
<td>1.65</td>
<td>2.21</td>
<td>2.50</td>
<td>1.65</td>
<td>1.28</td>
<td>1.88</td>
<td>2.21 3.10, 3.08^d</td>
</tr>
<tr>
<td>BaPo</td>
<td>1.45</td>
<td>1.93</td>
<td>2.28</td>
<td>1.45</td>
<td>1.01</td>
<td>1.59</td>
<td>1.98 -</td>
</tr>
<tr>
<td>BaSe$<em>{0.75}$O$</em>{0.25}$</td>
<td>1.58</td>
<td>2.10</td>
<td>2.18</td>
<td>-</td>
<td>1.50</td>
<td>2.04</td>
<td>2.13 -</td>
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<tr>
<td>BaS$<em>{0.25}$O$</em>{0.75}$</td>
<td>1.96</td>
<td>2.52</td>
<td>2.61</td>
<td>-</td>
<td>1.69</td>
<td>2.30</td>
<td>2.45 -</td>
</tr>
<tr>
<td>BaS$<em>{0.75}$Se$</em>{0.25}$</td>
<td>2.11</td>
<td>2.73</td>
<td>2.90</td>
<td>-</td>
<td>1.76</td>
<td>2.43</td>
<td>2.60 -</td>
</tr>
<tr>
<td>BaS$<em>{0.25}$Se$</em>{0.75}$</td>
<td>2.05</td>
<td>2.63</td>
<td>2.83</td>
<td>-</td>
<td>1.67</td>
<td>2.32</td>
<td>2.52 -</td>
</tr>
<tr>
<td>BaSe$<em>{0.75}$Te$</em>{0.25}$</td>
<td>1.90</td>
<td>2.39</td>
<td>2.62</td>
<td>-</td>
<td>1.53</td>
<td>2.08</td>
<td>2.32 -</td>
</tr>
<tr>
<td>BaSe$<em>{0.25}$Te$</em>{0.75}$</td>
<td>1.71</td>
<td>2.19</td>
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<td>-</td>
<td>1.33</td>
<td>1.84</td>
<td>2.14 -</td>
</tr>
<tr>
<td>BaTe$<em>{0.25}$O$</em>{0.75}$</td>
<td>1.68</td>
<td>2.07</td>
<td>2.16</td>
<td>-</td>
<td>1.34</td>
<td>1.78</td>
<td>2.06 -</td>
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<tr>
<td>BaTe$<em>{0.75}$O$</em>{0.25}$</td>
<td>1.01</td>
<td>1.36</td>
<td>1.44</td>
<td>-</td>
<td>0.92</td>
<td>1.30</td>
<td>1.40 -</td>
</tr>
</tbody>
</table>

^a Calculated energy gaps using unit cells; ^b Energy gap of X-X; ^c Ref. 55; ^d Ref. 56.

FIG. 3.9 Schematic diagram of the (200) plane in BaTe$_{0.75}$O$_{0.25}$. For the compound of BaX$_{0.75}$Y$_{0.25}$, barium atoms are located in the middles of four edges, X (one of the group VI elements) is located at the four corners and Y (substituting atom, same as X for a binary) is at the center of the (200) plane.
the GGA method. It also coincides with the empirical experience from other quantum calculations that the LDA method is believed to underestimate the energy gap and the GGA method decreases this error. For binaries, the GGA method is better than the LDA method in energy-gap calculations. Moreover, although it is difficult to predict the same results of energy gap as experiments from the GGA or LDA calculation, the trend behind the theoretical results is believed to be the same as the experimental results, which is helpful when searching for the factors influencing the electronic properties in barium chalcogenides.

3.2.2 Density of State and Partial Density of State

Figs. 3.6 and 3.7 present the theoretical results of the density of state (DOS) and partial density of state (PDOS) for all compounds using the GGA method. In Fig. 3.7, it is noted that, in barium chalcogenides, both conduction and valence bands come from the valence electrons of the group VI atoms. The contributions to DOS from s- and p-orbital valence electrons in barium are similar in all compounds. However, the contributions from the group VI atoms are different, depending on their environments in compounds. The wave functions of valence electrons in each group VI atom overlap with each other, which finally influences the electronic properties of the compounds. In the meantime, for binaries without oxygen, the contribution to DOS from each constituent atom is almost unchanged after the substitution. However, when a group VI atom substitutes the body-center oxygen atom in BaO, the PDOS of p-orbital valence electrons from the substituting atom is split into three peaks. This split is due to the strong interactions between the substituting atom and neighbor oxygen atoms. More detailed analyses about the influence of the oxygen element in barium chalcogenides will be addressed in following sections.
3.2.3 Charge Density

One purpose of this research is to find out the factors influencing the electronic properties of barium chalcogenides. As mentioned above, in barium chalcogenides, the chemical bonds between barium and the group VI elements are one of the important factors. Since theoretical charge densities can provide useful information on the chemical bonds in the compounds, the charge densities on the (200) planes for all compounds were calculated and given in Fig. 3.10. Because of the high-symmetry crystal structures of the compounds, the charge densities on the (200) plane can provide all necessary information about the distributions of the valence electrons in the compounds. Fig. 3.9 also gives a schematic diagram about the positions of all atoms on the (200) plane of BaTe$_{0.75}$O$_{0.25}$. For all other compounds in Fig. 3.10, the distribution of atoms on the (200) plane is similar to that of BaTe$_{0.75}$O$_{0.25}$, where the group VI atoms are at the four corners and center of the (200) plane and the barium atoms are at the middle of each boundary edge. From Fig. 3.10, it is interesting to find that, for all compounds not containing oxygen, the charge densities on the (200) plane change smoothly with slightly high charge densities found near the group VI atoms. However, for compounds containing oxygen, such as BaO, BaS$_{0.75}$O$_{0.25}$, BaS$_{0.25}$O$_{0.75}$, BaTe$_{0.75}$O$_{0.25}$, and BaTe$_{0.25}$O$_{0.75}$, high charge densities are always found near the oxygen atoms. Oxygen is known as the only oxidation element in the group VI elements and likely to attract electrons. Other elements, however, have less capability in attracting electrons. As a result, when oxygen atoms are introduced into compounds, electrons are likely to be localized by the oxygen atoms, which results in the high charge densities around the oxygen atoms. The results indicate that the chemical bonds between barium and oxygen are totally different from the bonds between barium and other group VI elements. Hence, the electrical properties of the
FIG. 3.10 Calculated charge densities on the (200) plane for all compounds using the GGA method.
compounds with oxygen are different from those without oxygen, which will be discussed below.

3.2.4 Chemical Bonds in Barium Chalcogenides

Usually, ionic, covalent, and metallic bonds are found in materials and as we know, Pauling electronegativity is a useful parameter to examine the properties of chemical bonds. It can provide rich information about the ionic characters in chemical bonds. Pauling electronegativity for a compound of $A_M B_N$ is defined by\(^{59}\)

$$f = 1 - \frac{N}{M} \exp \left[ -\frac{(X_A - X_B)^2}{4} \right], \quad 3.1$$

where, $X_A$ and $X_B$ are Pauling electronegativity of $A$ and $B$ elements, respectively. The value of Pauling electronegativity varies between 0 and 1. The higher the electronegativity is, the stronger the ionic character is found in the chemical bonds between $A$ and $B$, and vice versa. The Pauling electronegativities of all binaries are shown in TABLE 3.5.

<table>
<thead>
<tr>
<th></th>
<th>BaO</th>
<th>BaS</th>
<th>BaSe</th>
<th>BaTe</th>
<th>BaPo</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$</td>
<td>0.80</td>
<td>0.51</td>
<td>0.50</td>
<td>0.31</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Usually, if the electronegativity is larger than 0.75, the chemical bond is regarded as ionic bond and the ionic characteristics in chemical bonds is the most important part. For BaO, its electronegativity is 0.80, which means that the chemical bond between barium and oxygen is highly ionic. However, for other chemical bonds between barium and group VI elements (i.e., Ba–S, Ba–Se, Ba–Te, and Ba–Po), all calculated
Electronegativities are in the range of 0.27~0.51, which means that the ionic characteristics in these bonds are significantly weaker than that in Ba–O bond. It is well known from the periodic table of elements that, when one element forming chemical bonds with the elements from the same group, ionic part in chemical bonds usually decreases while the metallic part increases if the atomic number increases. As a result, the ionic part in chemical bonds decreases from Ba–O bond to Ba–Po bond. Polonium is known as a typical metallic element in group VI and Ba–Po are believed to be a highly metallic bond as compared to the bonds between barium and other group VI elements. Since the chemical bonds in compounds affect the electrons’ behaviours, different properties are expected to be found in the compounds containing and not containing oxygen, which have been observed in the former theoretical results.

3.2.5 Energy Gap

So far, the results from DOS, charge density, and electronegativity indicate that the properties of the compounds containing oxygen are different from those not containing oxygen because of the strong ionic characteristics in Ba–O chemical bond. Energy gap is another important property of semiconductors, which can be influenced by the chemical bonds in materials. It is, therefore, necessary to systematically study on the relationship between the energy gap and the characteristics of chemical bonds in barium chalcogenides. All calculated energy gaps using both the GGA and LDA methods (the energy gap of Γ-Γ) are listed in TABLE 3.4. The results are also plotted in Fig. 3.11 according to the LCs of compounds. It seems that the compounds containing oxygen can be roughly separated from the compounds not containing oxygen by a single line, as the dashed lines in Fig. 3.11. This observation is in agreement with the results from the theoretical DOS, charge-density and
 electronegativity calculations. Based on the experimental results of BaS, BaSe, and BaTe, Dalven\textsuperscript{60-62} summarized an empirical relationship that the energy gaps of barium chalcogenides have a linear relationship with $1/a^2$, where $a$ is the LC of a crystal. The results are shown in Fig. 3.12. Based on his conclusions, the theoretical energy gaps of binaries, using either the GGA or LDA method, are also studied and the results are shown in Fig. 3.12 too. It is found that, except BaO, the theoretical energy gaps are also linear with $100/a^2$, which agrees well with the empirical relationship summarized by Dalven. More interestingly, the slopes of the lines according to the theoretical results from the GGA and LDA methods are approximately equal to each other (1.62 for the GGA method and 1.60 for the LDA method) and slightly smaller than the slope of the line according to the experimental results (1.91). The energy gap of BaO deviates a lot from this linear relationship in both experimental and theoretical results. For obeying the same linear relationship, the theoretical energy gap of BaO should be 3.50 eV when using the GGA results (Fig. 3.12 (a)) and 3.18 eV when using the LDA results (Fig. 3.12 (b)). Both are much larger than the calculated results. Moreover, this linear relationship in binaries can also be extrapolated successfully to the ternaries not containing oxygen, while another linear relationship is found for all compounds containing oxygen. In Fig. 3.13, the energy gaps of all compounds, using both the GGA and LDA methods, are presented in terms of $100/a^2$. Two linear relationships are also indicated as the dashed and solid lines in Fig. 3.13. One is for the compounds containing oxygen and another is for the compounds not containing oxygen. The linear relationship for the compounds not containing oxygen seems to fit better than the results for the compounds containing oxygen. In brief, theoretical energy gaps from the GGA and LDA methods coincide with the experimental results that the energy gaps of barium chalcogenides is linear.
FIG. 3.11 Calculated energy gap vs lattice constant for all compounds using the (a) GGA and (b) LDA methods.
FIG. 3.12 Calculated energy gap $E_g$ vs $100/a^2$ for all binaries using the (a) GGA and (b) LDA methods. For comparison, some experimental results are also shown.
FIG. 3.13 Calculated energy gap vs $100/a^2$ for all compounds using the (a) GGA and (b) LDA methods.
with $1/\alpha^2$. Moreover, the results also indicate that the linear relationship for the compounds containing oxygen is different from the one for the compounds not containing oxygen. Again, this difference can be attributed to the special characteristics of Ba–O bonds in barium chalcogenides.

In Fig. 3.14, energy gaps are plotted in terms of the compound series. Different trends between the compounds containing and not containing oxygen are observed again in Fig. 3.14. For the compounds not containing oxygen (curves 1 and 2 in Figs. 3.14 (a) and 3.14 (b)), the energy gaps are linearly decreased if one chalcogen atom is substituted by other chalcogens atom with a larger radius or higher atomic number, and vice versa. However, for the compounds containing oxygen, this regulation does not hold any more. There is often a dip near the low oxygen content side. The results indicate that the oxygen atom in the compounds can be used to adjust the energy gaps in barium chalcogenides. Introduction oxygen into the compounds can first decrease the energy gap greatly and then increase it when the minimum gap is reached. The mechanism how oxygen influences the energy gaps of barium chalcogenides is unclear, but the special characteristics of Ba–O bonds must be one of the main reasons. This is because the chemical bonds in the barium chalcogenides determines the distribution of electrons in compounds and hence, influence the electrical properties such as the energy gaps.

Before the conclusions can be arrived, one point needs to be highlighted. Although all our theoretical results show that the characteristics of the chemical bonds in barium chalcogenides, especially Ba–O bond, lead to the different properties between the compounds containing and not containing oxygen, the mechanism is unclear and more experimental results are necessary. In the next chapter, a possible experimental
FIG. 3.14 Calculated energy gaps for different series of barium chalcogenides using the (a) GGA and (b) LDA methods. X and Y are two different group VI elements.
procedure for synthesizing barium chalcogenides with oxygen substitution will be proposed and then, theoretical calculations are performed to study the behavior of the oxygen atom on a binaries surface. The results provide some useful guides and suggestions for future experiments.

### 3.3 Summary

The properties of barium chalcogenides have been systematically studied using first-principles calculations based on the GGA and LDA methods. According to the results, the influence of chemical bonds on electronic properties was discussed. In barium chalcogenides, both the conduction and valence bands are formed by the valence electrons of the group VI atoms. Meanwhile, the results from calculated electronic properties indicated that the compounds containing oxygen always obey a different relationship from the compounds not containing oxygen. The results are attributed to the strong ionic characteristics in \( \text{Ba–O} \) as compared to the bonds between barium and other group VI elements, whose ionic part in bonds is not as important as that in \( \text{Ba–O} \). Finally, the energy gaps of barium chalcogenides can be adjusted by the oxygen concentration in the compounds. This observation would be useful to the design of devices, such as superlattice structures where semiconductors with various energy gaps are required.
Chapter 4: Simulated Study of Oxygen Absorption on BaTe(111) Surface

The calculated results in last chapter show that the oxygen concentration in barium chalcogenides is an important factor to determine the electronic properties of materials. By adjusting the oxygen concentration in the compounds, we can control the energy gaps accordingly. However, the conclusions are derived based on two assumptions. First, the crystal structures are changed slightly when the oxygen atom is introduced. In other words, the relative positions of all atoms are not changed except the distance between atoms. In fact, it is shown in Fig. 3.1 that, when an oxygen atom substitutes the body-center group VI element, the space group of a binary is changed from $F_{m\bar{3}}$ (NaCl structure) to $P_{m\bar{3}}$ (CsCl structure). Both are cubic structures and they can be regarded as similar to each other. Second, when an oxygen atom is introduced, it would substitute the group VI element in compounds. However, more investigations are necessary to determine the stable site for the oxygen atom to occupy, which is the objective of this chapter. With the considerations of these two assumptions as well as the fact that semiconductors are usually synthesized using thin film technology, an experimental procedure for further synthesis of barium chalcogenides is proposed as follows: a binary thin film is first formed on a substrate and then, oxygen is introduced into the thin film. However, two problems arise. The first one is to choose a binary thin film growing on a substrate according to the principle that an epitaxial film can be produced when the mismatch of the lattice parameters between a thin film and substrate is small. The second one is the way that
the oxygen atoms are absorbed onto the surface. Our purposes in this chapter are to systemically study the properties of a barium-chalcogenide surface and determine if oxygen can be used to tailor the band structures of compounds. The results are expected to provide useful guides for future experiments in developing new semiconductors of barium chalcogenides.

According to the first problem, lattice parameters of all binary barium chalcogenides are compared with some typical substrates such as Si, GaAs, and Al₂O₃. Fortunately, it is found that the lattice parameter of BaTe(111) matches that of Al₂O₃(0001) very well. Both primitive cells in the plane are equilateral parallelograms with the dimension of 4.942 Å for BaTe (corresponding to the crystal data that BaTe is in a cubic structure with the crystal structure of \( F_{\text{mm}} \), \( a = b = c = 7.000 \) Å) and 4.7589 Å for Al₂O₃ (corresponding to the crystal data that Al₂O₃ is in a hexagonal structure with the crystal structure of \( R_{\text{3}} \), \( a = b = 4.760 \) Å and \( c = 12.993 \) Å). The mismatch of the lattice pattern between BaTe(111) and Al₂O₃(0001) is as low as 3.7%. As a result, with more technological considerations, the BaTe(111) epitaxial film is in principle expected to be able to grow on an Al₂O₃(0001) substrate. Fig. 4.1 shows the distributions of atoms on the BaTe(111) and Al₂O₃(0001) planes.

Now, the remaining problem is to study the behaviors of oxygen atoms on the BaTe(111) surface using first-principles calculations. Finnis’s group in the Queen’s University of Belfast has made a great effort in applying first-principles calculations to study the properties of a surface (for details, please refer to their website and the papers published). Their work showed a great success in studying the system of the oxygen atoms on a binary alloy surface such as the NiAl(110) surface, which is
FIG. 4.1 The distributions of atoms on the ideal BaTe(111) surface with (a) side view and (c) top view for the first three layers (Layer A, B, and C) and the distribution of atoms on ideal Al₂O₃(0001) surface with (b) side view and (d) top view for the first three layers. Side-view schemas are shown using a 1×1 unit cell and top-view schemas are shown using a 2×2 unit cell. The blue, light-green, grey, and red balls represent the barium, tellurium, aluminium, and oxygen atoms, respectively. The dimensions of a basic vector are also shown for comparison.
similar to the system we are studying. Hence, we will follow their computational scheme to solve our research problems.

The key point for investigating the properties of a surface is the way to find the equilibrium positions of all atoms on the surface. In the following section, our computational scheme will be described in detail. The theoretical background for studying a surface structure using first-principles calculations will be also introduced.

### 4.1 Surface Energy of BaTe(111) Surface from First-Principles Calculations

In our calculations, the surface energies of supercells with various configurations (with or without defects) were first calculated by first-principles calculations. Here, supercell means the model of a surface for first-principles calculations. It is also known as a slab in literatures. After that, all obtained surface energies were compared with each other. The configuration with the minimum surface energy was regarded as the equilibrium one. In first-principles calculations, the surface energy of a supercell can be calculated only when some necessary valuables are acquired, as demonstrated in the following section.

#### 4.1.1 Surface Energy

The fundamental formula for the surface free energy of a special supercell used in a first-principles calculation is

\[
\sigma(T, p_{O_2}) = \frac{1}{A_s} (G_s - \sum_i \mu_i N_i).
\]  

4.1
where, $\sigma$ is the surface energy and it is a function of the temperature $T$ and oxygen partial pressure $p_{O_2}$. $G_s$ denotes the total Gibbs free energy of the slab and $A_s$ is the corresponding surface area of the slab. The index $i$ runs over all components in the slab (in our system, $i$ refers to barium, tellurium or oxygen). $\mu_i$ is the chemical potential of species $i$. $N_i$ is the number of atoms of species $i$ in supercell.

Usually, the effects of temperature or pressure on the Gibbs free energy of all solid materials are neglected because the corresponding corrections are small as compared to the temperature or pressure dependence of the vapor contribution in open systems. This implies that wherever the Gibbs free energy appears in the formula for bulk solids, it is just the total energy at the temperature of zero and pressure in a first-principles calculation. However, for oxygen, the temperature dependence of $\mu_O$ as well as its dependence on oxygen partial pressure, $p_{O_2}$, must be included since they are obviously the most important factors in the analysis. Another approximation made here is that there are no vapor molecules in the vacuum space of the supercell and few bulk defects are included in the interior of the supercell. The influence of the approximation on the final theoretical results is insignificant because the vapor can be very dilute and the concentration of defects can be so low that there are no bulk defects in the slab.

Meanwhile, during a first-principles calculation, a supercell with two surfaces is modelled in terms of the periodical properties. The interactions between these two surfaces can be neglected after compulsory convergent tests. However, only one surface participates in the oxidation. Another one is fixed at its geometry position since this surface is actually inside the bulk material in the original system. Therefore,
only the surface energy of the oxidized side is meaningful. The surface energy of the unrelaxed side, $\sigma_{\text{pure}}^{un}$, should be subtracted:

$$\sigma = \sigma_s - \sigma_{\text{pure}}^{un},$$  \hspace{1cm} 4.2

where $\sigma_s$ is the surface energy of the whole supercell calculated using Eq. 4.1, which includes the contributions from both oxidized and unrelaxed surfaces.

To find $\sigma_{\text{pure}}^{un}$, an additional calculation has to be performed using a stoichiometry supercell without surface defects, oxygen atoms, and relaxation run. In this case, $\sigma_{\text{pure}}^{un}$ can be expressed as

$$\sigma_{\text{pure}}^{un} = \frac{1}{2A_s}(G_s^{un} - \sum_i \mu_i N_i).$$  \hspace{1cm} 4.3

$G_s^{un}$ is the calculated Gibbs free energy of the supercell. Other parameters are the same as those in Eqs. 4.1 and 4.2.

Eq. 4.1 is the basic equation for calculating theoretical surface energy. Before applying this equation to a theoretical calculation, we still need to calculate the chemical potential of species $i$ in the system. In studied system with the oxygen on the BaTe(111) surface, we need calculate the chemical potentials of barium, tellurium, and oxygen.

4.1.2 Chemical Potentials of Barium, Tellurium, and Oxygen

The chemical potential of the constituent metal in an ordered alloy can be calculated in terms of the formation energies of the vacancy and antisite point defects, which was derived by Hagen and Finnis.\textsuperscript{65} For an ordered alloy with a formula of $A_mB_n$, the
chemical potentials of species $A$ and $B$ are expressed as:

\[
\mu_A = e_{AA} - e_{VA} + k_B T \log \left( \frac{c_{AA}}{c_{VA}} \right), \quad 4.4 \ a
\]
\[
\mu_B = e_{BB} - e_{VB} + k_B T \log \left( \frac{c_{BB}}{c_{VB}} \right), \quad 4.4 \ b
\]

where the subscript $V$ denote the point defect of vacancy, $c_{ij}$ is the concentration of $i$ on $j$’s sublattice, $e_{ij}$ is the energy of $i$ on a site of $j$, $T$ is the temperature, and $k_B$ is the Boltzmann constant.

Hagen and Finnis proceeded the derivation with an assumption that the concentration of the constitutional defect differed only by a small amount from its value at 0 K.\textsuperscript{65,66} The assumption is valid except at the concentrations very close to stoichiometry. It is accurate not only at low temperature but also at high temperature when a system is a few tenths of a per cent away from stoichiometry.

Based on the assumption, for a non-stoichiometry alloy of $A_{1-x}B_x$ where $x \approx \frac{n}{m + n}$, the chemical potentials of species $A$ and $B$ in an $A$-rich side are ($x < \frac{n}{m + n}$)

\[
\mu_A = \frac{n}{m + n} \left\{ e_{AB} + \frac{m}{n} e_{AA} + k_B T \log \left[ m(1-x) - nx \right] \right\}, \quad 4.5 \ a
\]
\[
\mu_B = e_{BB} + \frac{m}{m + n} \left\{ e_{AA} - e_{AB} - k_B T \log \left[ m(1-x) - nx \right] \right\}, \quad 4.5 \ b
\]

when the $A$ antisite is the constitutional defect, and

\[
\mu_A = e_{AA} + \frac{n}{m} \left\{ e_{VB} + k_B T \log \left[ \frac{m(1-x)}{nx} - 1 \right] \right\}, \quad 4.6 \ a
\]
\[
\mu_B = e_{BB} - e_{VB} - k_B T \log \left[ \frac{m(1-x)}{nx} - 1 \right], \quad 4.6 \ b
\]

when the vacancy in $B$ site is the constitutional defect.
The chemical potentials of species $A$ and $B$ in a $B$-rich side are ($x > \frac{n}{m+n}$)

$$
\mu_A = e_{AA} + \frac{n}{m+n} \left( e_{BB} - e_{BA} - k_B T \log[nx - m(1-x)] \right),
$$

4.7 a

$$
\mu_B = \frac{m}{m+n} \left( e_{BA} + \frac{n}{m} e_{BB} + k_B T \log[nx - m(1-x)] \right),
$$

4.7 b

when the $B$ antisite is the constitutional defect, and

$$
\mu_A = e_{AA} - e_{VA} - k_B T \log \left[ \frac{nx}{m(1-x)} - 1 \right],
$$

4.8 a

$$
\mu_B = e_{BB} + \frac{m}{n} \left( e_{VA} + k_B T \log \left[ \frac{nx}{m(1-x)} - 1 \right] \right),
$$

4.8 b

when the vacancy in $A$ site is the constitutional defect.

The chemical potentials of species of $A$ and $B$ can use the limiting values of Eqs. 4.5-4.8, which are simply obtained by setting the $k_B T$ term equal to zero at an $A$- or $B$-rich alloy.67

In the studied BaTe(111) surface, $m = n = 1$. To calculate the formation energy of an individual point defect such as $e_{AA}$, $e_{BB}$, $e_{AB}$, $e_{BA}$, $e_{VA}$, and $e_{VB}$, five models with 8 formula units with $2\times2\times2$ primitive cells each are constructed according to the perfect crystal (denoted as $M_8$), the defects of a barium atom in tellurium site (denoted as $M_{AB}$), a tellurium atom in barium site (denoted as $M_{BA}$), a vacancy in barium site (denoted as $M_{VA}$), and a vacancy in tellurium site (denoted as $M_{VB}$). The total energy of each model is given by

$$
E(M_8) = 8e_{AA} + 8e_{BB},
$$

4.9 a

$$
E(M_{AB}) = 8e_{AA} + 7e_{BB} + e_{AB},
$$

4.9 b

$$
E(M_{BA}) = 7e_{AA} + 8e_{BB} + e_{BA},
$$

4.9 c

$$
E(M_{VA}) = 7e_{AA} + 8e_{BB} + e_{VA},
$$

4.9 d

$$
E(M_{VB}) = 8e_{AA} + 7e_{BB} + e_{VB},
$$

4.9 e
where $E$ is the total energy calculated from each model, $A$ and $B$ denote barium and tellurium, respectively. After the convergence tests, the total energies and formation energies of point defects were calculated with a cutoff energy of 400 eV and 32 k points. All results are listed in TABLE 4.1.

**TABLE 4.1** Calculated formation energies of various point defects.

<table>
<thead>
<tr>
<th>Model</th>
<th>Total Energy (eV)</th>
<th>Formation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_A$</td>
<td>-7466.7135752</td>
<td>$e_{AA} + e_{BB} = -933.3391969$</td>
</tr>
<tr>
<td>$M_{AB}$</td>
<td>-7936.503656</td>
<td>$e_{AB} - e_{BB} = -469.7900904$</td>
</tr>
<tr>
<td>$M_{BA}$</td>
<td>-6983.3954167</td>
<td>$e_{BA} - e_{AA} = 483.3181585$</td>
</tr>
<tr>
<td>$M_{VA}$</td>
<td>-6756.9939494</td>
<td>$e_{VA} - e_{AA} = 709.7196258$</td>
</tr>
<tr>
<td>$M_{VB}$</td>
<td>-7236.2457172</td>
<td>$e_{VB} - e_{BB} = 230.467858$</td>
</tr>
</tbody>
</table>

From the formation energies of various point defects, the constitutional defect in the BaTe(111) surface can be theoretically determined. If $e_{AB} - e_{AA} - 2e_{VB} < 0$, the constitutional defect in the Ba-rich surface is the barium antisite; otherwise the tellurium vacancy is the constitutional defect. Similarly, if $e_{BA} - e_{BB} - 2e_{VA} < 0$, the constitutional defect in the Te-rich surface is the tellurium antisite; otherwise the barium vacancy is the constitutional defect. Based on the criteria, it is shown from TABLE 4.1 that the constitutional defects are the tellurium vacancy in the Ba-rich surface and the tellurium antisite in the Te-rich surface. The chemical potentials of barium and tellurium in eV per atom are

$$
\mu_{Ba} = -702.87134 + k_B T \log \frac{1 - 2x}{x}, \quad 4.10 \text{ a}
$$

$$
\mu_{Te} = -230.46786 - k_B T \log \frac{1 - 2x}{x}, \quad 4.10 \text{ b}
$$
in the Ba-rich surface. In the Te-rich surface, they can be expressed as

\[
\mu_{Ba} = -708.32868 - \frac{1}{2} k_B T \log(2x - 1), \quad 4.11 \text{ a}
\]

\[
\mu_{Te} = -225.01052 + \frac{1}{2} k_B T \log(2x - 1). \quad 4.11 \text{ b}
\]

The chemical potentials of barium and tellurium on the Ba- or Te-rich BaTe(111) surface are shown in Fig. 4.2 as a function of the tellurium content, \(x\), at 500 K. Fig 4.2 shows that the chemical potentials are almost constant except in the vicinity of \(x = 0.5\), where Eqs. 4.10 and 4.11 are not applicable at the point. As a result, it is convenient to take the limiting values of Eqs. 4.10 and 4.11 as the chemical potentials of barium and tellurium for following discussions.

On the other hand, to calculate the chemical potential of oxygen, its partial pressure and the temperature must be considered since oxygen is a gas phase. Its chemical potential can be described using a standard ideal gas expression

\[
\mu_o(p_{O_2}, T) = \mu^0_o(p^0_{O_2}, T) + \frac{1}{2} k_B T \log(p_{O_2} / p^0_{O_2}), \quad 4.12
\]

where the superscript “0” denotes quantities at the standard oxygen pressure \(p^0_{O_2}\), \(\mu_o(p_{O_2}, T)\) and \(\mu^0_o(p^0_{O_2}, T)\) are the oxygen chemical potentials at \(p_{O_2}\) and \(p^0_{O_2}\), respectively. However, a theoretical calculation of the chemical potential of a gas phase is a great challenge. In Felice’s work,\(^{68}\) the chemical potential of hydrogen was taken to be equal to the energy per hydrogen atom in molecular \(H_2\), which was an upper bound on its true value. In Wang’s work,\(^{69}\) the chemical potential of oxygen was treated as the energy by dissociating an oxygen molecule and taken from experiments. In Finnis’s work,\(^{70}\) another scheme was suggested, where a thermodynamic cycle such as the reaction for the formation of \(Al_2O_3\) at the standard
FIG. 4.2 Chemical potentials of barium and tellurium vs the tellurium content at 500 K. The gaps on the curves in the vicinity of \( x = 0.5 \) appear because Eqs. 4.10 and 4.11 are not applicable at the point.

Partial oxygen pressure was chosen:

\[
2\text{Al}(s) + \frac{3}{2}\text{O}_2(g) \leftrightarrow \text{Al}_2\text{O}_3(s).
\]

Hence, the balance of the Gibbs free energy for the reaction is

\[
g^0_{\text{Al}_2\text{O}_3}(T) = 2\mu^0_{\text{Al}}(T) + 3\mu^0_{\text{O}}(T) + \Delta G^0_{\text{Al}_2\text{O}_3}(T), \tag{4.13}
\]

where \( g^0_{\text{Al}_2\text{O}_3} \) is the Gibbs free energy of the bulk alumina per formula unit, which can be calculated from first-principles calculations at \( T = 0 \) K. A similar way can be employed to calculate the Gibbs free energy of aluminum, \( \mu^0_{\text{Al}} \cdot \Delta G^0_{\text{Al}_2\text{O}_3}(T) \) is the formation energy which can be looked up in the tables of thermodynamic data. Then
the chemical potential of oxygen is written as

\[
\mu_0(p_{O_2}, T) = \frac{1}{3}(g_{d,t,O_2}^0(T) - 2\mu_{d,t}^0(T) - \Delta G_{d,t,O_2}^0(T)) + \frac{1}{2}k_BT \log(p_{O_2}/p_{O_2}^0). \tag{4.14}
\]

However, Finnis also mentioned that his choice of a \(\alpha\)-alumina to calculate the chemical potential of oxygen was arbitrary.\(^66\) In fact, the calculation of oxygen chemical potential using first-principles methods is still a great challenge. In this work, since we only concern with the difference of the surface energy between two configurations and only one oxygen atom is introduced into each slab, \(\mu_0(p_{O_2}, T)\) can be simply regarded as a reference data. The final conclusion is fixed no matter how large \(\mu_0(p_{O_2}, T)\) is because the surface energy of each supercell is

\[
\sigma(x, T, p_{O_2}) = \frac{1}{A_s}(G_s - \sum_{i}^{i} \mu_i N_i) - \frac{N_O \mu_O}{A_s}. \tag{4.15}
\]

\(N_O\) is the number of the oxygen atoms in the supercell. In our case, \(N_O = 1\). As a result, the change of surface energy between two different configurations is

\[
\Delta \sigma = \sigma_1 - \sigma_2
\]

\[
= \left[ \frac{1}{A_s}(G_s - \sum_{i}^{i} \mu_i N_i) - \frac{N_O \mu_O}{A_s} \right] - \left[ \frac{1}{A_s}(G_s - \sum_{i}^{i} \mu_i N_i) - \frac{N_O \mu_O}{A_s} \right]
\]

\[
= \left[ \frac{1}{A_s}(G_s - \sum_{i}^{i} \mu_i N_i) \right] - \left[ \frac{1}{A_s}(G_s - \sum_{i}^{i} \mu_i N_i) \right]. \tag{4.16}
\]

Eq. 4.16 shows that the difference of the surface energy between two configurations is not a function of the chemical potential of oxygen. Hence, it is convenient to set the chemical potential of oxygen as zero, \(\mu_O(p_{O_2}, T) = 0\). We can avoid the errors arising when calculating its chemical potential from first-principles calculations. In following calculations, if not specifically declared, the surface energy is calculated with the assumption of \(\mu_O(p_{O_2}, T) = 0\).
4.1.3 Supercell of BaTe(111) Surface and Its Optimization

4.1.3.1 Supercell

According to Figs. 4.1 (a) and (c), BaTe(111) has the stacking sequence of AB CD EF AB . . . . In each layer, there are either barium atoms or tellurium atoms with the barium and tellurium layer alternatively. The patterns in each layer are same while with a displacement in the $\frac{1}{3}[1\bar{1}0]$ direction between every two neighbor layers. To make a clear observation, we redraw the BaTe(111) surface in Fig. 4.3, where a 2×2 unit cell used for the first-principles simulations and four possible sites (denoted as sites 1, 2, 3, and 4) for absorbing oxygen are also indicated. Because the environments of each barium or tellurium layer are same, the stacking sequence therefore can be simplified as AB AB . . . rather than AB CD EF AB . . . . Then, the surface of BaTe(111) can be either a barium (barium termination) or tellurium layer (tellurium termination). Because one of the objectives of our calculations is to find out whether the oxygen atom can substitute the tellurium atom on the BaTe(111) surface, all calculations were performed using more rigorous conditions where a surface with the barium termination was studied. In this case, all tellurium atoms are hidden under the barium surface and a formation of Te–O bond on the BaTe(111) surface became very difficult. During the calculations, a 2×2 supercell with four barium atoms on the surface was chosen to reduce the interactions between the defects in the neighbor supercells. Meanwhile, to find out the relaxed structure of a surface, the symmetry of a supercell was reduced to the monoclinic structure $P_1$ with the space group of 1. Each supercell in relaxation calculations consisted of five layers. The atoms on the first four layers (The barium surface was the first layer.) were movable and the atoms
FIG. 4.3 Top view of the ideal BaTe(111) surface. A 2×2 supercell for simulations is also described with a solid line. Grey circles represent the barium atoms and white circles represent the tellurium atoms. The largest grey circles show the first (surface) layer, the white circles correspond to the second (layer below the surface) layer and the smallest grey circles describe the third layer. The fourth layer, a tellurium layer appears in the same positions below the surface barium layer (the largest grey circles). Four possible sites for adsorbing oxygen are also indicated, where site 1 refers to Ba top site, site 2 is Ba-Ba bridge site, site 3 is 4Ba site, and site 4 is 3Ba-Te site.

on the bottom layer were fixed as they were in the bulk crystal. Hence, there were totally twenty atoms with twelve barium atoms and eight tellurium atoms in each supercell.

4.1.3.2 Supercell Configurations

Two stages were considered when studying the adsorption of oxygen on the BaTe(111) surface. The first stage was the initial adsorption of an oxygen atom onto the clean BaTe(111) surface. The second one was the movement of the oxygen atom on the BaTe(111) surface after the initial stage of adsorption.
During the first stage, the supercell of a clean BaTe(111) surface without any defects was employed with one oxygen atom on one of the possible absorption sites. There are four possible sites for an oxygen atom to be absorbed, i.e., Ba top, Ba-Ba bridge, 4Ba, and 3Ba-Te site, which are denoted as sites 1 to 4 respectively and shown in Fig. 4.3. Hence, four slabs were prepared in our calculations with one oxygen atom on these four possible absorption sites. The preferred site for an oxygen atom to stay was the one with the lowest surface energy.

In the second stage, point defects such as vacancies and/or antisites were introduced into each slab with one oxygen atom staying at the preferred absorption site. In our calculation, all studied configurations in supercells were determined according to all possible defects on a surface.

All studied configurations and their notations in the calculations are listed in TABLE 4.2. The final analyses were carried out based on the calculated surface energy according to each configuration.

### 4.1.3.3 Surface Relaxation

The relaxation calculation, also known as optimization, is to determine the equilibrium positions of all atoms on the surface. Usually, the relaxation is conducted by means of the Broyden-Fletcher-Goldfarb-Shano (BFGS) method. However, the results in Finnis’ work showed that the BFGS method was insufficient for a surface relaxation because, in this method, the system merely moved to the nearest configuration and couldn’t always find the structures with the lowest surface energy. However, the results from the BFGS method can be improved by choosing a better
TABLE 4.2 Notations of different configurations used in the present study. The point defects are denoted as \( Y_z^{(i)} \), which means species \( Y \) (Ba, Te, O or vacancy V) on sublattice \( Z \) (Ba or Te) in layer \( i \) (the surface is the first layer). In each supercell, only one oxygen atom is introduced.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Point Defect in Supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_{a_{pof}} )</td>
<td>no defect, no oxygen atom, no optimization run, perfect barium surface</td>
</tr>
<tr>
<td>( B_{a_{BFGS}} )</td>
<td>no defect, no oxygen atom, optimized supercell using only the BFGS(^a) run</td>
</tr>
<tr>
<td>( B_{a_{MD}} )</td>
<td>no defect, no oxygen atom, optimized supercell using the BFGS followed by the MD(^b) run</td>
</tr>
<tr>
<td>( T_{e_{pof}} )</td>
<td>no defect, no oxygen, no optimizing run, perfect tellurium surface</td>
</tr>
<tr>
<td>( D_{o1} )</td>
<td>without any defects, one oxygen atom on site 1 (Ba top site)(^c)</td>
</tr>
<tr>
<td>( D_{o2} )</td>
<td>without any defects, one oxygen atom on site 2 (Ba-Ba site)(^c)</td>
</tr>
<tr>
<td>( D_{o3} )</td>
<td>without any defects, one oxygen atom on site 3 (4Ba site)(^c)</td>
</tr>
<tr>
<td>( D_{o4} )</td>
<td>without any defects, one oxygen atom on site 4 (3Ba-Te site)(^c)</td>
</tr>
<tr>
<td>( D_{\alpha} )</td>
<td>( V_{Ba}^{(1)} )</td>
</tr>
<tr>
<td>( D_{\beta} )</td>
<td>( V_{Te}^{(2)} )</td>
</tr>
<tr>
<td>( D_{\gamma} )</td>
<td>( O_{Ba}^{(1)} )</td>
</tr>
<tr>
<td>( D_{\delta} )</td>
<td>( O_{Te}^{(2)} )</td>
</tr>
<tr>
<td>( D_{\epsilon} )</td>
<td>( Te_{Ba}^{(1)} )</td>
</tr>
<tr>
<td>( D_{\zeta} )</td>
<td>( Ba_{Te}^{(2)} )</td>
</tr>
<tr>
<td>( D_{\eta} )</td>
<td>( Te_{Ba}^{(1)} + O_{Te}^{(2)} )</td>
</tr>
<tr>
<td>( D_{\theta} )</td>
<td>( V_{Te}^{(2)} + Te_{Ba}^{(1)} )</td>
</tr>
<tr>
<td>( D_{\iota} )</td>
<td>( V_{Ba}^{(1)} + Ba_{Te}^{(2)} )</td>
</tr>
<tr>
<td>( D_{\kappa} )</td>
<td>( Te_{Ba}^{(1)} + Ba_{Te}^{(2)} )</td>
</tr>
</tbody>
</table>

\(^a\) BFGS (Broyden-Fletcher-Goldfarb-Shano); \(^b\) MD (molecular dynamics); \(^c\) Please refer to Fig. 4.3 for the positions of sites 1 to 4.
starting configuration, where the positions of all atoms are near the optimization ones. Thus, a molecular-dynamics (MD) run is found to be necessary before the optimization running using BFGS.

In CASTEP, the Car and Parrinello’s scheme is employed for a MD run because the method can (1) compute the ground-state electronic properties of large and/or disordered systems at the level of state-of-the-art electronic structure calculation and (2) perform *ab initio* MD simulations where the only assumptions are the validity of classical mechanics to describe ionic motion and the Born-Oppenheimer approximation to separate nuclear and electronic coordinates. The advantages of the MD run are that it probes the collective motions of all atoms in a supercell and that it is suitable for searching the optimization configurations. After the MD run, the results are treated as the starting configurations for the BFGS run. The employed strategy can acquire better relaxation structures than those only using the BFGS run.

In brief, when performing a surface relaxation, we first prepared a certain supercell as described in Section 4.1.3.1. The supercell corresponded to one of the configurations listed in TABLE 4.2. Then, we performed a MD run at 500 K with a time step of 1.00 fs and a total time of 0.5 ps (There were 500 steps in a MD run, which were widely adopted when doing a quantum MD run.). A cutoff energy of 300 eV and 1 k point were employed for the MD run. After the MD run, we collected the positions of all atoms and performed a BFGS optimization. The scheme used here, as mentioned by Finnis, still did not “guarantee arriving at the global minimum, but in many cases, a significant drop in energy has been achieved”. The positions of all atoms after the BFGS run were regarded as the equilibrium ones and fixed for further convergence tests and total-energy calculations.
4.1.3.4 Convergence Tests

The convergence tests were performed in terms of (1) the vacuum separation of the periodically repeated slabs, (2) the slab thickness, (3) the k-point mesh, and (4) the cutoff energy. Since all slabs in the calculations were of similar dimension as well as the number of atoms, all convergence tests were conducted using the slab corresponding to the configurations of \( \text{Da} \) and/or \( \text{Do3} \). We first fixed the positions of all atoms in a slab using the results from the MD and BFGS runs. Then we adjusted the vacuum size between the two surfaces (the top and bottom layers of the slab) and the thickness of the slab. The convergence tests were necessary to make sure that the interactions between the top and bottom layers in the slab were very weak. Fig. 4.4 shows the calculated surface energies at various vacuum separations. It is shown that when the vacuum is larger than 9 Å in a slab, the energy difference is small enough for a convergence. As a result, a vacuum of 9 Å is accepted for the following convergence tests and total-energy calculations. In the second step, the total energies were calculated with the number of layers in the slab of \( \text{Da} \) or \( \text{Do3} \) changed from five to nine. Further increasing the number of the layers in a slab is beyond the computational capacities available in our lab. All calculated results are listed in TABLE 4.3. It seems that the difference of the energies between the seven- and nine-layer slabs is 0.01458 J/m² for \( \text{Da} \) and 0.01782 J/m² for \( \text{Do3} \). Both reach the convergence results. Therefore, for our studied system, a seven-layer slab is necessary for a convergence result. In next convergent and total-energy calculations, a slab with seven layers and a vacuum of 9 Å will be used.

During the first two-step convergence test, a cutoff energy of 500 eV and 9 k points corresponding to a \( 3 \times 3 \times 3 \) k-point mesh were employed to reduce the errors caused by
FIG. 4.4 Calculated surface energies at various vacuum separations. The surface energy according to the supercell with a vacuum of 3 Å is set as zero.

TABLE 4.3 Calculated surface energies for supercells according to the configurations of Da and Do3 with various numbers of layers.

<table>
<thead>
<tr>
<th>Layers in Supercell</th>
<th>Da</th>
<th>Do3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Energy (eV)</td>
<td>Surface Energy (J/m^2)</td>
</tr>
<tr>
<td>5</td>
<td>-10486.47798</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>-14219.55285</td>
<td>0.05338</td>
</tr>
<tr>
<td>9</td>
<td>-17952.98668</td>
<td>0.03880</td>
</tr>
</tbody>
</table>

a The surface energy of the five-layer slab is set as zero; b The surface energy of the five-layer slab is set as zero.
insufficient computational parameters in the total-energy calculations. In the next steps, the slabs for the convergence tests were fixed to have seven-layer atoms and a vacuum of 9 Å between the bottom and top surfaces, while different cutoff energies as well as k points were tried for calculations. The supercell according to the configuration of $\text{Do3}$ was employed and the total energies were calculated at different cutoff energies and k points. After that, the surface energy from each calculation was employed for a comparison. All results are listed in TABLE 4.4.

**TABLE 4.4** Calculated total energies and surface energies with different cutoff energies and k points on the BaTe(111) epitaxial film.

<table>
<thead>
<tr>
<th>Cutoff Energy (eV)</th>
<th>k points</th>
<th>Total Energy (eV)</th>
<th>Surface Energy $^a$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>9</td>
<td>-14444.8549521</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>9</td>
<td>-14449.9343657</td>
<td>-0.96185</td>
</tr>
<tr>
<td>400</td>
<td>9</td>
<td>-14450.1649888</td>
<td>-1.00552</td>
</tr>
<tr>
<td>500</td>
<td>9</td>
<td>-14450.1292245</td>
<td>-0.99875</td>
</tr>
<tr>
<td>500</td>
<td>5</td>
<td>-14450.1243112</td>
<td>-0.99782</td>
</tr>
<tr>
<td>500</td>
<td>2</td>
<td>-14450.1029445</td>
<td>-0.99377</td>
</tr>
</tbody>
</table>

$^a$ The surface energy calculated with a cutoff energy of 200 eV and 9 k points is set as zero.

It is shown that when calculating with a cutoff energy of 400 or 500 eV and 9 k points, the energy difference is less than 0.007 J/m$^2$. If calculating with 5 or 9 k points and a cutoff energy of 500 eV, the energy difference is less than 0.001 J/m$^2$. As a result, a calculation with a cutoff energy of 500 eV and 9 k points can obtain convergence results. Considering the results from the first- and second-step convergence tests, in the total-energy calculations, a slab was necessary to be prepared with seven-layer atoms and a vacuum of 9 Å, while its total energy was calculated with a cutoff energy.
of 500 eV and 9 k points based on the GGA-PW91 functional.

### 4.2 Results and Discussion

All calculated total energies and their corresponding surface energies are listed in TABLE 4.5. The chemical potentials of barium and tellurium equal to the limiting values of Eqs. 4.10 and 4.11 by setting the $k_B T$ term equal to zero. Surface energies were calculated with the assumption that the chemical potential of oxygen was zero.

#### 4.2.1 Equilibrium Sites for Oxygen Absorption on Clear BaTe(111) Surface

Before the diffusion of oxygen onto the BaTe(111) surface, the oxygen atom is absorbed to a clean surface first. As mentioned before, there are four possible sites for the oxygen atom to sit on the BaTe(111) surface, as shown in Fig. 4.3. The one with the lowest surface energy is the equilibrium site. From the results of calculated surface energies in TABLE 4.5, it is shown that site 3 (4Ba site) is the equilibrium one for oxygen to sit on the BaTe(111) surface since its theoretical surface energy is the lowest. The theoretical results indicate that when an oxygen atom is introduced to the clean BaTe(111) surface, it prefers to occupying site 3 first.

Meanwhile, for comparison, the surface energies of the clear BaTe(111) surfaces without oxygen atoms absorbed were also calculated using three different supercells. The first one was conducted without any optimization, the second one was optimized only using a BFGS run, and the last one was optimized using both the MD and BFGS runs. All calculated surface energies, denoted as $Ba_{pef}$, $Ba_{BFGS}$, and $Ba_{MD}$, are also
### TABLE 4.5 Calculated total energies and surface energies according to different configurations on the BaTe(111) epitaxial film.

<table>
<thead>
<tr>
<th>Notationa</th>
<th>Total Energy (eV)</th>
<th>Surface Energyb (J/m²)</th>
<th>Point Defect in Supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ba-Rich Side</td>
<td>Te-Rich Side</td>
</tr>
<tr>
<td>$Ba_{pbf}$</td>
<td>-14008.5158737</td>
<td>0.16460</td>
<td>4.70932</td>
</tr>
<tr>
<td>$Ba_{BFGS}$</td>
<td>-14008.9011688</td>
<td>0.09164</td>
<td>4.63636</td>
</tr>
<tr>
<td>$Ba_{MD}$</td>
<td>-14009.3160039</td>
<td>0.01308</td>
<td>4.55780</td>
</tr>
<tr>
<td>$Te_{pbf}$</td>
<td>-12093.23224</td>
<td>5.43654</td>
<td>1.30286</td>
</tr>
<tr>
<td>$Do1$</td>
<td>-14448.6528489</td>
<td>-84.11794</td>
<td>-79.52204</td>
</tr>
<tr>
<td>$Do2$</td>
<td>-14447.2480776</td>
<td>-83.84893</td>
<td>-79.25303</td>
</tr>
<tr>
<td>$Do3$</td>
<td>-14450.1292245</td>
<td>-84.40066</td>
<td>-79.80476</td>
</tr>
<tr>
<td>$Do4$</td>
<td>-14449.6286846</td>
<td>-84.30481</td>
<td>-79.70891</td>
</tr>
<tr>
<td>$Da$</td>
<td>-13741.3459284</td>
<td>-83.16463</td>
<td>-79.71771</td>
</tr>
<tr>
<td>$Dβ$</td>
<td>-14219.5528483</td>
<td>-84.48380</td>
<td>-78.73893</td>
</tr>
<tr>
<td>$Dγ$</td>
<td>-13738.7719297</td>
<td>-82.67172</td>
<td>-79.22480</td>
</tr>
<tr>
<td>$Dδ$</td>
<td>-14218.2817872</td>
<td>-84.24040</td>
<td>-78.49552</td>
</tr>
<tr>
<td>$Dε$</td>
<td>-13966.8400179</td>
<td>-82.10826</td>
<td>-79.81031</td>
</tr>
<tr>
<td>$Dζ$</td>
<td>-14919.7719594</td>
<td>-84.07983</td>
<td>-77.18598</td>
</tr>
<tr>
<td>$Dη$</td>
<td>-13738.8411423</td>
<td>-82.6850</td>
<td>-79.23805</td>
</tr>
<tr>
<td>$Dθ$</td>
<td>-13736.9864727</td>
<td>-82.32981</td>
<td>-78.88289</td>
</tr>
<tr>
<td>$Dν$</td>
<td>-14212.8202683</td>
<td>-83.19454</td>
<td>-77.44966</td>
</tr>
<tr>
<td>$Dκ$</td>
<td>-14439.1858757</td>
<td>-82.30506</td>
<td>-77.70916</td>
</tr>
</tbody>
</table>

a The detail of each model is also explained in TABLE 4.2; b The chemical potential of oxygen is assumed to be zero.
listed in TABLE 4.5. It is shown that the lowest surface energy is the one optimized after both the MD and BFGS runs. The results indicate that the optimization scheme employed in this study can really find an equilibrium structure of a surface with a lower surface energy than those using only the BFGS optimization or not using any optimization. Although it is difficult to claim that the optimized structures after the MD and BFGS runs are definitely the same as the original system which can be observed in experiments, the theoretical results from the present scheme are believed to approximate the ground states better than others used in first-principles calculations since it can find a lower surface energy in a surface. As we know, the stable structure would be the one with the lowest thermal energy.

Since the chemical potential of oxygen is assumed to be zero to reduce the error coming from its calculation using first-principles methods, for the slab with oxygen inside in TABLE 4.5, the difference of surface energy between two configurations is important for discussions.

4.2.2 Point Defects on BaTe(111) Surface with Oxygen Absorbed

All calculated surface energies according to the configurations with various defects inside are listed in TABLE 4.5 based on the Ba- or Te-rich BaTe(111) surface.

On the Ba-rich BaTe(111) surface, the tellurium sublattice cannot be fully occupied by tellurium. From TABLE 4.5, it shows that only the vacancy (configuration $D\beta$) or oxygen atom (configuration $D\delta$) would occupy the tellurium sites since their calculated surface energies are the lowest. It is slightly difficult for barium to occupy the tellurium site on the Ba-rich BaTe(111) surface (configuration $D\zeta$). As we know,
oxygen and tellurium are group VI elements and both of them have the ability to attract two electrons to occupy their unfilled orbits. Therefore, the tellurium site can be easily occupied by oxygen and the calculated surface energy is low. Meanwhile, barium is one of typical metals in group II and its chemical properties are different from the one in group VI. As a result, the surface energy would be increased if barium occupied the tellurium sublattice. However, tellurium is also known as a metal in group VI. Its ability to attract electrons is much weaker than oxygen. Hence, the total effect is that the surface energy only becomes slightly high after the tellurium sublattice occupied by barium. In the mean time, for the barium sublattice on the Ba-rich BaTe(111) surface, it is easy to be fully occupied by barium atoms. As a result, it is impossible for vacancy, tellurium, or oxygen to occupy the barium sites, such as the configurations of $D_\alpha$, $D_\gamma$, and $D_\varepsilon$, whose surface energies are very high as shown in TABLE 4.5. Moreover, for the configurations with this kind of defects, such as the configurations of $D_\eta$ and $D_\theta$, although there is another stable defect like the vacancy or oxygen atom on the tellurium site in the slabs, the calculated surface energies are still very high, and the configurations are unstable as compared to others in TABLE 4.5.

On the other hand, on the Te-rich BaTe(111) surface, the barium sublattice cannot be fully occupied by barium atoms. The calculated surface energies indicate that the vacancy (configuration $D_\alpha$) or tellurium atom (configuration $D_\varepsilon$) can take the place of the barium site while a substitution of the barium site by an oxygen atom (configuration $D_\gamma$) increases the surface energy greatly. As discussed above, both tellurium and barium are metals and a substitution of a barium site by a tellurium atom doesn’t change the chemical properties of BaTe(111) surface greatly. However,
the chemical properties of oxygen are totally different from barium. For oxygen, it has six valence electrons at the outmost orbits and it is very easy for him to attract another two electrons to occupy the unfilled orbits. For barium, as one of the group II elements, it is likely to lose two valence electrons and form a bivalent cation in materials. As a result, when an oxygen atom takes the place of the barium site, the charge balance on the surface is destroyed, which would increase the surface energies of the system. In the mean time, for the tellurium sublattice, it can be fully occupied by tellurium atoms. A substitution of the tellurium site by a vacancy, oxygen or barium atom can increase the surface energy greatly and hence, the defect becomes unstable, such as the configurations of $D\beta, D\delta$, and $D\zeta$.

The results in TABLE 4.5 also indicate that the atom radius is an unimportant factor in determining the surface energy of the BaTe(111) surface. For a bivalence ion with coordination number of six, the radii are 1.40 Å for oxygen, 2.21 Å for tellurium, and 1.49 Å for barium, respectively. Although the ion radii of oxygen is much smaller than that of tellurium while approximates to that of barium, an oxygen atom can occupy the tellurium site on the Ba-rich BaTe(111) surface but cannot occupy the barium site on the Te-rich one.

It is necessary to be pointed out again that, due to the limited computational power of modern computers, we can only study the point defects in the first two layers in a supercell with seven-layer atoms. The model is, therefore, still very small as compared with an original system. In the mean time, we can only study the vacancy and antisite during the calculations, which may not fully describe the real situations on a surface. How to predict the properties of a large system from the theoretical results using a small model is one of the great challenges in first-principles
calculations. It requires more powerful supercomputers or breakthroughs in the theory of first-principles calculations. Nevertheless, a lot of successes have been achieved in the research of theoretical calculations. It is shown from our results that oxygen atoms can substitute the tellurium sites on the Ba-rich BaTe(111) surface after they are absorbed onto the clean surface at site 3 (4Ba site). An effort to experimentally investigate the oxygen absorption on the BaTe(111) surface is still worth doing to search new II-VI semiconductors.

4.3 Summary

The behavior of oxygen on the BaTe(111) surface has been studied using first-principles calculations. Both the MD and BFGS runs were employed for the surface-structure optimization. The scheme is better than the method only using the BFGS or not using any relaxation since the scheme can obtain a lower surface energy in a supercell while with much more computational time. During the calculations, convergence tests were performed compulsorily according to the vacuum size, number of layers, cutoff energy and k point. The first two tests were to reduce the scale of the supercell and the interactions between two surfaces in the supercell. Another two tests were to choose corresponding computational parameters. To study the behavior of oxygen on the BaTe(111) surface with or without defects, a supercell with seven layers and a vacuum of 9 Å is the basic requirements. During the total-energy calculations, a cutoff energy of 500 eV and 9 k points are necessary. An oxygen atom on the clean BaTe(111) surface was first studied. After that, the BaTe(111) surface with defects was studied. When an oxygen atom is introduced to a clean BaTe(111) surface, there are four possible sites for oxygen to sit on. The
calculated results showed that oxygen prefers site 3 (4Ba site) since the surface energy is the lowest when oxygen is in this site. In the meantime, the results according to different configurations with defects inside showed that a vacancy or oxygen atom on a tellurium site is stable on the Ba-rich BaTe(111) surface while a vacancy or tellurium atom on a barium site is stable on the Te-rich BaTe(111) surface. It is worthwhile to perform an experimental synthesis of a Ba-rich BaTe(111) thin film with oxygen absorption to find new II-VI semiconductors in barium chalcogenides.
Chapter 5: Conclusions and Future Works

5.1 Conclusions

The electronic properties of barium chalcogenides have been systematically studied using first-principles calculations based on both the GGA and LDA methods. The lattice constants from the GGA and LDA calculations match the experimental results very well while the results from the GGA method are better than those from the LDA method. Both conduction and valence bands in band structures of barium chalcogenides are formed by the valence electrons of the group VI elements. The energy gaps of barium chalcogenides follow two linear relationships with $1/a^2$ ($a$ is the lattice constant) depending on whether oxygen is a constituent element. Moreover, when oxygen atoms are in compounds, high charge densities are always found near them. Special trends for the compounds containing and not containing oxygen have been observed in calculated electronic properties. It is attributed to the special chemical bonds between barium and the group VI elements. Pauling electronegativities show that the Ba–O bond is an ionic bond. But in bonds between barium and other group VI elements, the ionic parts are not so important. As a result, oxygen would restrict the movement of valence electrons in barium chalcogenides and thus, influence their electronic properties. Finally, with the presence of oxygen in compounds, the energy gaps can be adjusted in terms of the oxygen concentration in barium chalcogenides.
The behavior of oxygen on a BaTe(111) surface was also studied from first-principles calculations. Both the MD and BFGS optimizations were employed to search the relaxation structures on the surface. The scheme is better than that with only BFGS or without any optimization. Convergence tests according to vacuum size, the number of layers, cutoff energy and k point were performed when preparing the supercells or calculating total energies. For the BaTe(111) surface with one oxygen atom, a supercell with seven-layer atoms and a vacuum of 9 Å is a basic requirement. In total-energy calculations, a cutoff energy of 500 eV and 7 k points were used to obtain convergence. An oxygen atom on the clean BaTe(111) surface was first studied. After that, the defects in the BaTe(111) surface are studied. When an oxygen atom is introduced on the clean BaTe(111) surface, there are four possible sites for it to sit on. The theoretical surface energies show that oxygen prefers to occupying site 3 (4Ba site in Fig. 4.3). Meanwhile, the calculated surface energies show that a vacancy or oxygen atom on a tellurium site is stable on the Ba-rich BaTe(111) surface while a vacancy or tellurium atom on a barium site is stable on the Te-rich BaTe(111) surface. The theoretical results indicate that it is possible for an oxygen atom to substitute the tellurium site on the Ba-rich BaTe(111) surface. It is, therefore, possible to synthesize new II-VI semiconductors by diffusing oxygen on the BaTe(111) surface.

5.2 Future Works

First, in Chapter 4, only a few typical configurations were chosen for first-principles calculations and final discussions. However, to make a comprehensive analysis, the theoretical results according to more configurations are desired. Hence, one of the future works is to perform the theoretical calculations by considering more possible
configurations such as $V_{Ba}^{(1)} + O_{Te}^{(2)}$ and $Ba_{Te}^{(2)} + O_{Ba}^{(1)}$.

Meanwhile, in our work, only point defects in first two layers are considered when prepare our supercell for calculation and each supercell only have seven-layer atoms inside. Hence, if more powerful computers are available, all theoretical calculations can be performed using much larger supercells with more atoms inside. More complex defects, such as the linear defects of dislocation in surfaces, can be also considered when building the supercells for first-principles calculations. The results can enrich our understanding of the properties on a surface.

Finally, a theoretical calculation can declare its final success only when its conclusions can be proved by experiments. At the same time, II-VI semiconductors have drawn more and more research interests. Our results also demonstrate that barium chalcogenides can be good candidates for wide-band-gap semiconductors. Therefore, it is worthwhile an attempt to experimentally study the properties of barium chalcogenides and their possible applications to wide-band-gap semiconductors.
Bibliography:


1660-1665.


42 (1990), 9357-9364.


Appendix A:

All calculated total energies at various LCs are shown as follows.

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340 eV → 36×36×36
0.03 → 6×6×6 → 10

400 eV → 36×36×36
0.03 → 6×6×6 → 10

*a* Calculated results using the GGA method; *b* Calculated results using the LDA method; The last row in each table is the parameters for calculations, where the first line is the cutoff energy corresponding to Fast Fourier Transforms (FFT) and the second line is the k points corresponding to Monkhorst-Pack mesh. The units of LC and total energy are Å and eV, respectively.