INVESTIGATION OF PROPERTIES IN BARIUM CHALCOGENIDES USING 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.

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,[1] many experimental and theoretical results have been reported for chalcogenides such as zinc chalcogenides,[2,3] cadmium chalcogenides,[4] and beryllium chalcogenides.[5-7] 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.[8] 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,[9-10] tin,[11] and antimony chalcogenides.[12]

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

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

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.

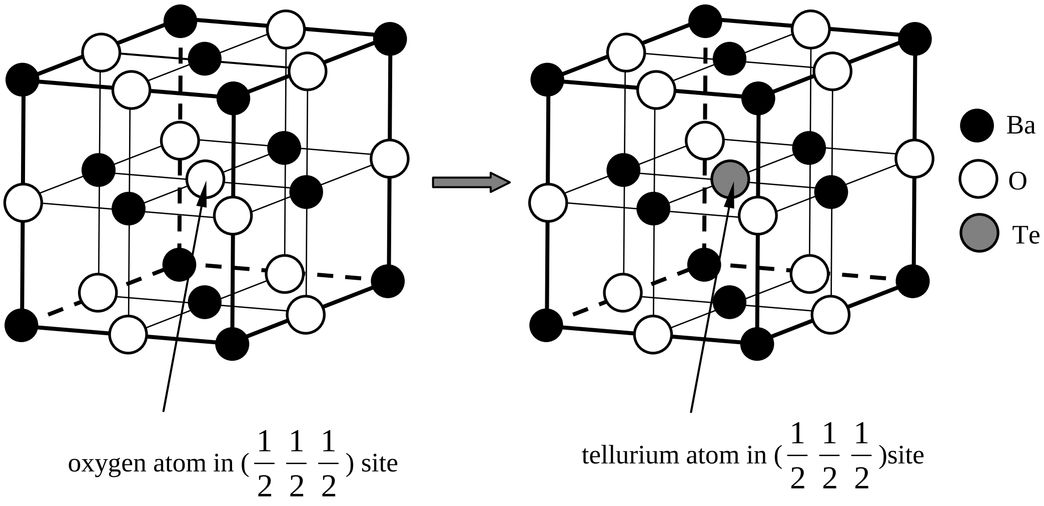
3.1 Structural Properties in Barium Chalcogenides

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, $F_{m\bar{3}m}$) to 221 (B2 structure, CsCl type, $P_{m\bar{3}m}$). 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 artifical 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



(a) (b)

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 3.1 All studied ternary compounds.

Name	$\mathbf{BaS_{0.75}O_{0.25}}$	$\mathbf{BaS_{0.25}O_{0.75}}$	$\mathbf{BaS_{0.75}Se_{0.25}}$	$\mathbf{BaS_{0.25}Se_{0.75}}$
Substitution Operator	S in BaS by O	O in BaO by S	S in BaS by Se	Se in BaSe by S
Name	$\mathbf{BaSe_{0.75}Te_{0.25}}$	$\mathbf{BaSe_{0.25}Te_{0.75}}$	$\mathbf{BaTe_{0.25}O_{0.75}}$	$\mathbf{BaTe_{0.75}O_{0.25}}$
Substitution Operator	Se in BaSe by Te	Te in BaTe by Se	O in BaO by Te	Te in BaTe by O

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

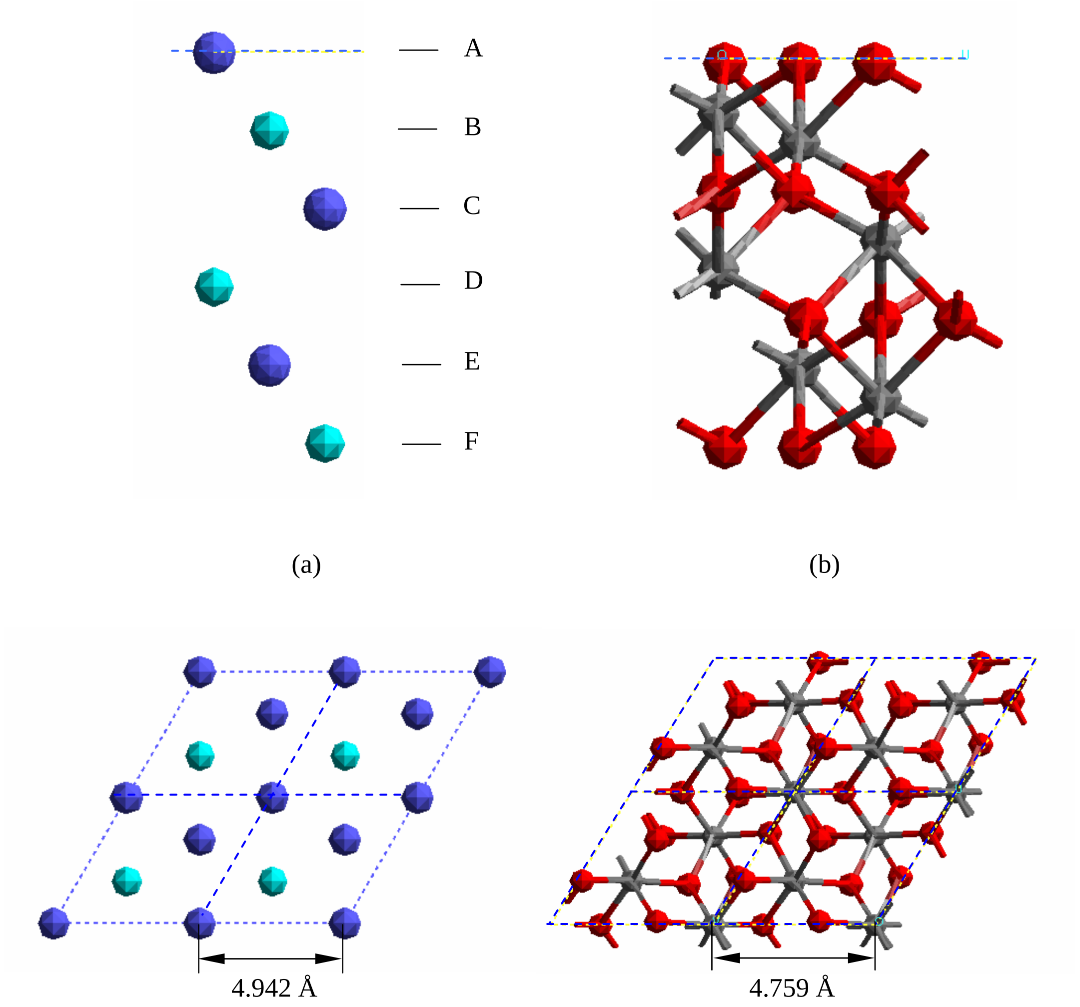
The properties of barium chalcogenides have been systematically studied using first-principles calculations based on the GGA and LDA methods. According to the results, the influence of chemical bonds on electronic properties was discussed. In barium chalcogenides, both the conduction and valence bands 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 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 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 $F_{m\bar{3}m}$ (NaCl structure) to $P_{m\bar{3}m}$ (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 Al_2O_3. Fortunately, it is found that the lattice parameter of BaTe(111) matches that of Al_2O_3(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[30] that BaTe is in a cubic structure with the crystal structure of $F_{m\bar{3}m}$, $a = b = c = 7.000$ Å) and 4.7589 Å for Al_2O_3 (corresponding to the crystal data[63] that Al_2O_3 is in a hexagonal structure with the crystal structure of $R_{\bar{3}c}$, $a = b = 4.760$ Å and $c = 12.993$ Å). The mismatch of the lattice pattern between BaTe(111) and Al_2O_3(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 Al_2O_3(0001) substrate. Fig. 4.1 shows the distributions of atoms on the BaTe(111) and Al_2O_3(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



(a) (b)

(c) (d)

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 Al_2O_3(0001) surface with (b) side view and (d) tope 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[64]

$$\sigma(T, p_{O_2}) = \frac{1}{A_s}(G_s - \sum_i \mu_i N_i)\,. \qquad 4.1$$

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.

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