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Electronic properties of barium chalcogenides from first-principles calculations: Tailoring wide-band-gap II-VI semiconductors

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Electronic properties of barium chalcogenides were systematically studied using density functional theory computations, based on both generalized gradient approximation and local density approximation functionals. Different linear relationships are observed between theoretical band gap and $1/a^2$ (where a is lattice constant) for barium chalcogenides containing oxygen and not containing oxygen, respectively. An abnormal behavior of electronic properties are found for compounds containing oxygen. The effects are attributed to the special properties of Ba–O bonds, which is different from other chemical bonds between barium and chalcogen atoms. Pauling electronegativity indicates that only Ba–O bonds are highly ionic bonds, and theoretical charge densities also show that electrons would be restricted to oxygen atoms when oxygen is in compound. The results reveal that it is possible to adjust the band gap significantly in barium chalcogenide by introducing oxygen atoms into its lattice for the gap tailoring of wide-band-gap II-VI semiconductors.

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I. INTRODUCTION

II-VI chalcogenide compounds have attracted increasing interest due to their potential applications in light-emitting diodes (LEDs) and laser diodes (LDs). Ever since the first demonstration of a blue-green-emitting laser using ZnSe by Haase *et al.*,[1] experiments and first-principles calculations were reported for chalcogenides including zinc chalcogenides,[2] cadmium chalcogenides,[3] and beryllium chalcogenides.[4] It is expected that chalcogenide may provide new II-VI candidates, complementing the well known IV and III-V semiconductors, for the fabrication of various electrical and optical devices.[5] On the other hand, the VI group elements experience a change from nonmetallic (O) to metallic (Po), which provides a good system for the analysis of general chemical trends among chalcogenides, as demonstrated in recent publications in lead-,[6] tin-,[7] and antimony-chalcogenides.[8]

Until now, only a few reports on first-principles calculations are available in the study of the pressure-induced phase transformation in barium chalcogenides.[9–12] No systematic research on the electronic properties of barium chalcogenides have been reported, although these compounds may lead to some unique optoelectronic properties due to their diverse bond characteristics, and simple rock-salt crystal structure (B1 structure, $F_{m\bar{3}m}$) which makes first-principles computations more affordable. Experiments show that the B1 structure is stable until 10 GPa for BaO,[13] 6.5 GPa for BaS,[13] 6.0 GPa for BaSe,[14] and 4.8 GPa for BaTe.[15] A studyof 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 semiconductors for various applications, including a blue-emitting laser. This paper reports our efforts in understanding this important system using the density functional theory (DFT) calculations.

II. FIRST-PRINCIPLES CALCULATIONS

All calculations involved in this study were performed using the Cambridge Serial Total Energy Package (CASTEP), where a plane-wave pseudopotential (PWP) scheme based on DFT was applied. Both the generalized gradient approximation (GGA-PW91)[16] and the local density approximation (LDA) were used for calculating the exchange-correlation energy. The valence electronic configuration during the calculation was $5s^2 5p^6 6s^2$ for barium and $ns^2 np^4$ for chalcogens. Ultrasoft pseudopotential[17] for every atom was employed in this research. The total energies of various barium chalcogenides with B1 structure at different volumes were calculated first. For accuracy, 300 eV cutoff energy was adopted to make sure that there were enough plane waves involved in wave-function expansion. Meanwhile, 10 special k points corresponding to the $6 \times 6 \times 6$ Monkhorst-Park mesh[18] were used for Brillouin zone integration. All parameters have been tested for convergence. The total energies as a function of volume were then fitted by Birch-Murnaghan's equation of state[19] to obtain equilibrium lattice constant a_0. A unit cell for theoretical calculation is shown in Fig. 1.

To study the effects of chemical bonds in the II-VI semiconductors, a partial substitution of the chalcogen atom in binary by other chalcogen atom was conducted and therefore new chemical bonds between barium and chalcogens were formed in compounds. For example, when the body-centered Te atom in BaTe (one of the high-symmetry points in compound) was substituted by an O atom, some Ba–Te chemical bonds in BaTe were replaced by Ba–O bonds (see Fig. 1(b)). After each substitution, the total energy for each new system was then calculated at different volume and the results were fitted to the equation of state to obtain the equilibrium lattice constant a_0.

After total-energy calculations, some important electronic properties, such as band structure and charge density, were calculated at the theoretical equilibrium volume using both the GGA and LDA methods.

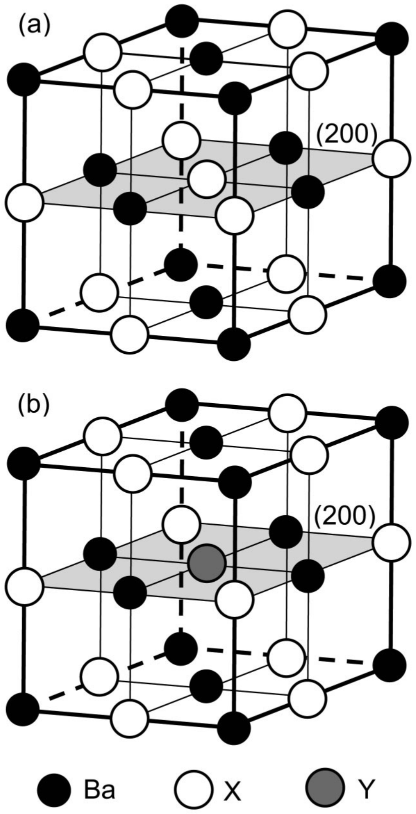


FIG. 1. Schematic unit cells of (a) BaX, $F_{m\bar{3}m}$, and (b) $BaX_{0.75}Y_{0.25}$, $P_{m\bar{3}m}$ for the theoretical calculation. X and Y are two different chalcogen atoms. The (200) plane in unit cell is shadowed.

TABLE I. Calculated and experimental equilibrium lattice constants a_0 (Å) of barium chalcogenides.

	a_0 (Å)		
Name	GGA	LDA	EXP[a]
BaO	5.562	5.454	5.520
BaS	6.407	6.276	6.374
BaSe	6.640	6.477	6.600
BaTe	6.989	6.869	7.000
BaPo	7.046	6.950	7.119
$BaS_{0.25}O_{0.75}$	5.839	5.720	
$BaS_{0.75}O_{0.25}$	6.245	6.126	
$BaS_{0.25}Se_{0.75}$	6.584	6.427	
$BaS_{0.75}Se_{0.25}$	6.462	6.328	
$BaSe_{0.25}Te_{0.75}$	6.909	6.777	
$BaSe_{0.75}Te_{0.25}$	6.745	6.585	
$BaTe_{0.25}O_{0.75}$	6.113	5.988	
$BaTe_{0.75}O_{0.25}$	6.783	6.650	

[a] References 9–12 and the references therein.

III. RESULTS AND DISCUSSION

The total energies of barium chalcogenides as a function of their volume were calculated using the GGA and LDA methods, and were fitted to the equation of state using the least-squares method. The equilibrium lattice constants a_0 were obtained and shown in Table I.

Table I shows that the calculated equilibrium lattice constants for binaries are in good agreement with the experiments; especially the results obtained using the GGA method. The results are also consistent with the empirical experience that LDA often underestimates lattice constant while GGA reduces this error considerably. For compounds after substitution, the volume of the unit cell should be increased if the atom in the cell is substituted by a larger atom, and decreased if by a smaller one. As a result, the lattice constant of $BaTe_{0.75}O_{0.25}$ is smaller than that of BaTe and larger than that of BaO. Similar results are found for other compounds in our calculations.

Band structures and charge densities were calculated using both the GGA and LDA methods and the results show similar patterns. In Fig. 2, the typical band structures of BaO, BaTe, $BaTe_{0.25}O_{0.75}$, and $BaTe_{0.75}O_{0.25}$ are presented and other compounds are of similar patterns. The band structures show that all compounds are direct band-gap semiconductors with a minimum gap at the Γ point. Meanwhile, the energy difference at Γ and X points in the conduction band is so small that the indirect transitions in these materials are also possible. In Table II, the direct band gap of each compound at the Γ point is shown. For comparison, experimental results of binary compounds[20] are also listed. However, no experimental data for ternary compounds can be found at this time. All band gaps calculated using the GGA and LDA methods are found to be smaller than the experimental ones, as ex-

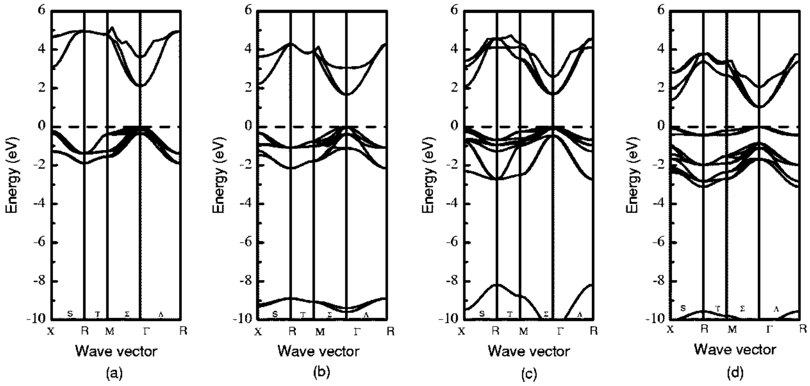


FIG. 2. Calculated band structures using the GGA method for (a) BaO, (b) BaTe, (c) $BaTe_{0.25}O_{0.75}$, and (d) $BaTe_{0.75}O_{0.25}$. All these compounds are direct band-gap semiconductors, which are also found in all other compounds calculated using either the GGA or LDA method.

TABLE II. Calculated band gaps E_g (eV) at the Γ point and the experimental band gaps of barium chalcogenides.

	E_g (eV)		
Name	GGA	LDA	EXP
BaO	2.09	1.67	3.88[a], 4.10[b]
BaS	2.17	1.83	3.88[a], 3.90[b]
BaSe	2.02	1.63	3.58[a], 3.60[b]
BaTe	1.65	1.28	3.08[a], 3.10[b]
BaPo	1.45	1.01	
$BaS_{0.25}O_{0.75}$	1.96	1.69	
$BaS_{0.75}O_{0.25}$	1.58	1.41	
$BaS_{0.25}Se_{0.75}$	2.05	1.67	
$BaS_{0.75}Se_{0.25}$	2.11	1.76	
$BaSe_{0.25}Te_{0.75}$	1.71	1.33	
$BaSe_{0.75}Te_{0.25}$	1.90	1.53	
$BaTe_{0.25}O_{0.75}$	1.68	1.34	
$BaTe_{0.75}O_{0.25}$	1.01	0.92	

[a] Reference 20. All experimental results were deduced from an optical absorption spectrum of polycrystalline films at −160 °C.

[b] Reference 21. All experimental results were deduced from an optical absorption spectrum of polycrystlaline films at liquid air temperature (−196 °C) except BaO which was measured at room temperature.

pected. The calculated band gaps for BaS (2.1 eV,[10] 2.30 eV[11]), BaSe (1.8 eV,[10,12] 2.01 eV[11]), and BaTe (1.4 eV,[10] 1.58 eV,[11] 1.45 eV[12]) available in literature, support our calculated results. For BaS, BaSe, BaTe, and BaPo, band gaps are decreased with the increasing of atomic number, which can be attributed to the characteristics of bonds in compounds. Usually, ionic bonds, covalence bonds, and metallic bonds are found in II-VI semiconductors. For barium chalcogenides, with the increase of atomic number, the ionic characteristic decreases and the metallic one increases from a Ba–O bond to a Ba–Po bond, accompanied by a decrease of the band gap.

TABLE III. Pauling electronegativity (f) of chemical bonds between the barium and chalcogen atom.

	Ba–O	Ba–S	Ba–Se	Ba–Te	Ba–Po
f	0.80	0.51	0.50	0.31	0.27

Using experimental data of BaS, BaSe, and BaTe, Dalven summarized an empirical relationship that band gaps of barium chalcogenides were linear with $1/a^2$, where a was the lattice constant of crystal.[22] It is shown in Fig. 3 that the theoretical band gaps of BaS, BaSe, BaTe, and BaPo, calculated using either the GGA or LDA method, are also linear with $1/a^2$, except BaO. Interestingly, the slope of the line according to the theoretical results is similar to that of the experimental results. For BaO, to obey the same linear relationship, the band gap has to be 3.50 eV when using the GGA method [Fig. 3(a)] and 3.18 eV when using the LDA method [Fig. 3(c)], respectively, which are greatly larger than the calculated results. Moreover, the linear relationship can also be extended to ternary compounds not containing oxygen [solid lines in Figs. 3(b) and 3(d)]. However, for compounds containing oxygen, another linear relationship has to be followed, as the dashed lines describe in Figs. 3(b) and 3(d). In Fig. 4, we also present the results of band gaps versus compound series. From Fig. 4, it seems that the analy-

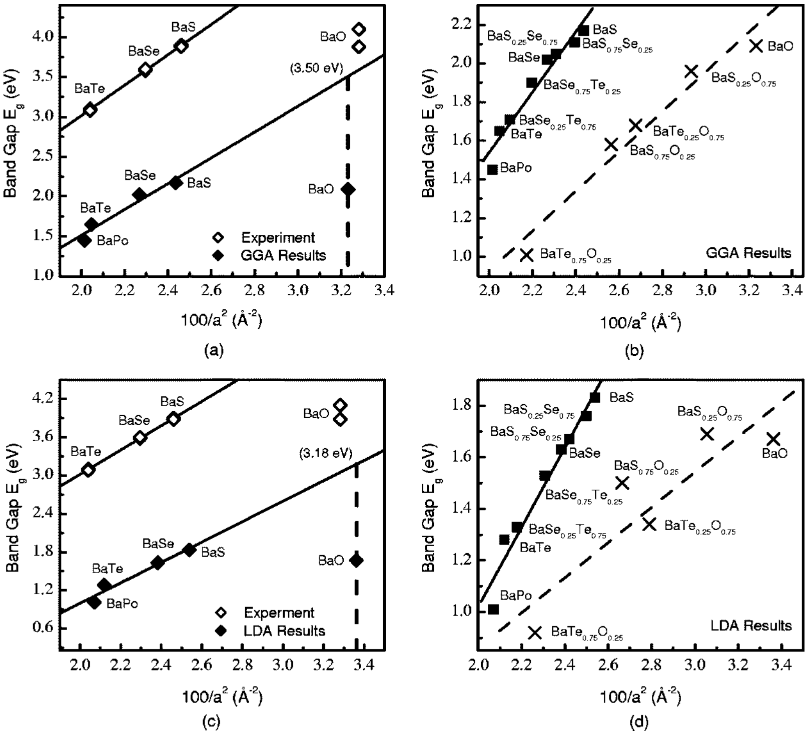
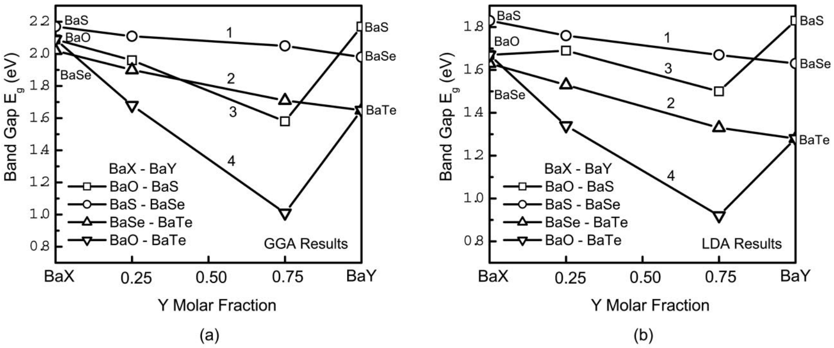


FIG. 3. The band gap vs $100/a^2$ where a is the equilibrium lattice constant. The results for binary compounds are listed in (a) and (c). The results for all compounds are listed in (b) and (d). The results in (a) and (b) are calculated using the GGA method, in (c) and (d) using the LDA method. The white diamond in (a) and (c) indicates the experimental result, and the dark one in (a) and (c) indicates the calculated result. The dark square in (b) and (d) indicates a compound not containing oxygen, and the cross indicates a compound containing oxygen.



(a) (b)

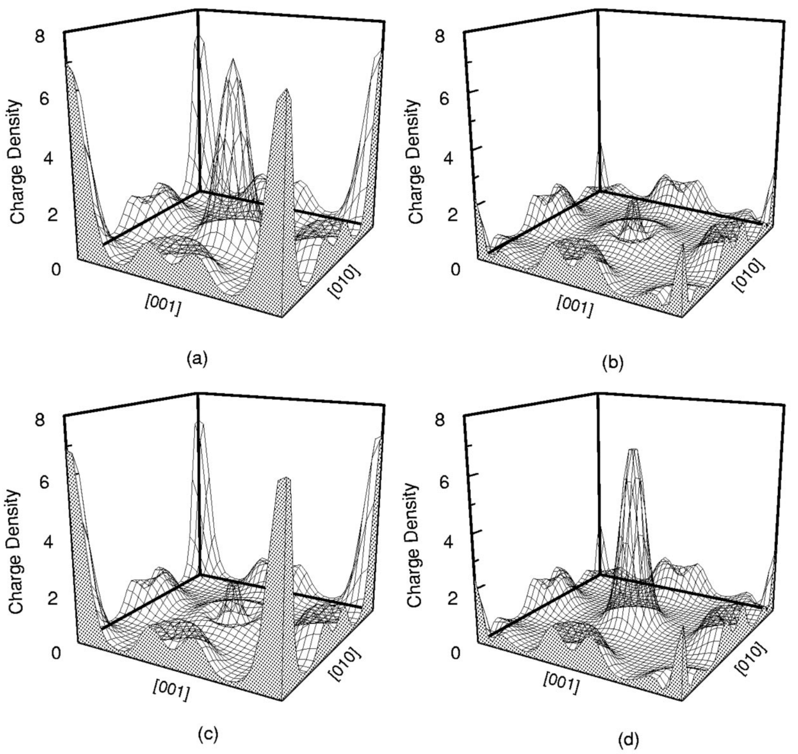
FIG. 4. Calculated band gap vs compound series (a) using the GGA method and (b) using the LDA method. X and Y in (a) and (b) are two different chalcogen elements, respectively. A dip is found near the low oxygen side for the series containing oxygen, while a linear relationship is found for compounds not containing oxygen.

sis can be made again according to the compounds containing and not containing oxygen. For those compounds without oxygen [curves 1 and 2 in Figs. 4(a) and 4(b)], the band gaps would be linearly decreased if the substitution is employed by introducing another chalcogen atom with a larger radius or higher atom number. Otherwise, the band gap would be linearly increased. However, for compounds containing oxygen, this regulation does not hold. There is often a dip in the curves close to the low oxygen content side [curves 3 and 4 in Figs. 4(a) and 4(b)].

The special trend for oxygen-contained compounds can be attributed to the high ionic characteristics in Ba–O, which is worth discussing more. Since Pauling electronegativity[23] can be used to study the ionic characteristic in chemical bonds, we calculate the Pauling electronegativity for all binaries with B1 structure. The Pauling electronegativity for a compound of $A_M B_N$ is described by Eq. (1) and the results are shown in Table III.

$$f = 1 - \frac{N}{M} \exp\left\{ - \frac{(X_A - X_B)^2}{4} \right\}. \tag{1}$$

Here, X_A and X_B are Pauling electronegativity of elements A and B, respectively. The electronegativity of Ba–O is 0.80, which means that the bond between the barium and oxygen atom is highly ionic. However, the electronegativities of bonds between barium and other chalcogen elements (i.e., Ba–S, Ba–Se, etc.) are in the range of 0.27–0.51 and the ionic characteristic is significantly weaker than that in Ba–O. It is known from the periodic table of elements that, when forming chemical bonds with the elements in the same group, with the increase of atom number, the ionic part in chemical bonds decreases while the metallic part increases. Hence the ionic part in chemical bonds decrease from Ba–O bonds to Ba–Po bonds, as mentioned above. It is the characteristics of chemical bonds that result in the different electronic properties between barium chalcogenides containing oxygen and not containing oxygen as the chemical bonds can affect the distribution of valence electrons or their movement in compounds.



(a) (b) (c) (d)

FIG. 5. Calculated charge density in the (200) plane using the GGA method, (a) BaO, (b) BaTe, (c) $BaTe_{0.25}O_{0.75}$, and (d) $BaTe_{0.75}O_{0.25}$. Chalcogen elements seat in the corners and the middle of the plane (especially for substituting atom in ternary compounds). Ba atoms seat in the middle of the four edges. A schematic diagram of the (200) plane is shown in Fig. 1. Extremely high charge density is found near oxygen atoms. Similar results are found in all compounds calculated using either the GGA or LDA method.

Because the bond characteristics in compounds can essentially affect the distribution of valence electrons in compounds, the charge densities of valence electrons in all compounds are calculated using both the GGA and LDA methods. In Fig. 5 the charge densities of BaO, BaTe, $BaTe_{0.25}O_{0.75}$, and $BaTe_{0.75}O_{0.25}$ calculated using the GGA method are shown. It is indicated in Fig. 5 that in BaTe, the compound without an oxygen atom, the charge density changes smoothly all around the compound with a slightly higher density found near the Te atom. However, when oxygen atoms are introduced, most valence electrons are restricted by oxygen atoms, which results in an extremely high charge density near oxygen atoms, such as $BaTe_{0.25}O_{0.75}$ or $BaTe_{0.75}O_{0.25}$ in Fig. 5. The localization of electrons near oxygen atoms can be found in all barium chalcogenides we calculated using either the GGA or LDA method. The results can be explained according to the fact that in ionic bonds, the valence electrons are removed from one atom and attached to another atom resulting in positive and negative ions in compounds, while in metal bonds, valence electrons can move more easily throughout compounds.

IV. CONCLUSIONS

The electronic properties of barium chalcogenides are systemically studied using DFT calculations (both GGA and LDA functional). According to the results, the influence of chemical bonds on electronic properties in semiconductors is discussed. It is indicated from the results that the electronic properties of compounds containing oxygen atoms always obey a different relationship from the compounds not containing oxygen atoms. The results are essentially attributed to the bond characteristics between barium and chalcogen atoms. The Ba–O bonds are characterized as high ionic bonds. But all other bonds between barium and chalcogen atoms seem to be of similar properties. The influence from the ionic part in these bonds decreases while the one from the metallic part increases, resulting in the different electronic properties between the compounds containing and not containing oxygen. Moreover, for barium chalcogenides containing oxygen, the band gap may be adjusted by varying its oxygen contents, especially at the lower oxygen content side. The results may aid in the design of new II-VI semiconductors.

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