Electronic and optical properties of Janus monolayers MoXB₂ (X=S, Se): first-principles prediction

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Abstract. By means of comprehensive first-principles calculations, we studied the geometric structure, the stability and electronic properties of the new two-dimensional (2D) Janus MoXB₂ (X=S, Se) monolayers. Our calculations demonstrated that the predicted Janus MoXB₂ monolayers are all stable semiconductors with direct band gap. In this paper, we focus on impacts upon the electronic and optical properties of the MoXB₂ monolayers under the different biaxial strains. With the compressive stress increases, the MoXB₂ monolayers would become indirect band gap semiconductors, and then behave as semimetal. While under tensile strain, MoXB₂ still maintain direct band gap. In addition, the optical calculation shows that biaxial strain leads to blue shifts in the optical absorption and reflectivity. The result indicates that MoXB₂ may be promised nano candidate materials in optoelectronic devices.

1 Introduction

Since graphene was prepared, two-dimensional atomic thickness materials have attracted wide attention in nanomaterials due to their excellent physical and chemical properties [1,2]. Graphene has excellent properties, such as high specific surface area, high conductivity, good thermal stability, excellent mechanical strength, adjustable electrical and superior optical and superficial properties. Therefore, 2D monolayer materials were considered significant in the design of new optoelectronic devices [3–12]. Due to graphene is a semimetal, the band gap is zero, the conduction band and the valence band intersect in the Brillouin region, so the band gap is difficult to open, which has led to many barriers in applying to electronic devices and the field of semiconductors. Therefore, the new two-dimensional semiconductor materials with band gap are the focus of researchers. Recently, the Janus structures are particular interesting because they possess many new properties that could not be found in those of pristine materials [13–22].

The 2D materials are extremely sensitive to structural perfection and geometric symmetry plays a key role in determining their electronic properties. The breaking of mirror symmetry in Janus structures can result in many new properties [23,24]. In recent years, a variety of Janus monolayers have been predicted by breaking of mirror symmetry, such as MoSSe [25,26] monolayer, which the top-layer S atoms of MoS₂ are fully replaced by Se atoms. Because the hexagonal boron layers in MoB₄ monolayer [27] have been proved to be stable, based on density functional theory (DFT) and using a first-principles calculation in this framework, we designed the new 2D Janus material, namely the MoXB₂ (X=S, Se) monolayers, which are direct band gap semiconductors. MoXB₂ (X=S, Se) monolayers can be viewed as the complete replacement of the boron layer in the bottom layer of MoB₄ monolayer by X atoms to break the mirror symmetry. Afterwards, we systematically investigated their stability and electronic properties. Interestingly, they have good dynamic and mechanical stabilities and tunable electronic properties as a result of exceptional structural characteristics. Thus, we studied the influence of appropriate biaxial strain on the electronic and optical properties of the MoXB₂ monolayers. These calculated electronic and optical characteristics indicate that the MoXB₂ monolayers are suitable for making optoelectronic devices.

2 Computational methods

First-principles calculations were performed using the density functional method (DFT) implemented in the Vienna ab initio simulation package (VASP) [28–30]. For the exchange and correlation functional, we use the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [31]. The cutoff energy is set to 500 eV. The convergence criteria for energy and force are set to 1 × 10⁻⁵ eV and 0.03 eV/Å, respectively. The vacuum space along the z-direction is set to 15 Å to minimize artificial interactions between neighboring layers. A Monkhorst-Pack mesh of 9 × 9 × 2 k-points was used to sample the Brillouin zone of the unit cell for geometry optimizations and properties calculations [32]. The phonon calculations are carried out using Phonopy program implementing density functional perturbation theory (DFPT) method [33].
3 Results and discussion

3.1 Structures and stability of the MoXB2 (X=S, Se) monolayers

The optimized structures of MoXB2 (X=S, Se) monolayers can be regarded as a hexagonal boron lattice covered by a triangular X layer and a Mo atom under the center of the B hexagonal. Meanwhile, B atoms are arranged in a very slightly buckled honeycomb lattice. Within each unit cell [marked by the dashed line in Figure 1a], it contains two B atoms and one Mo atom and one X atom. The MoXB2 monolayers can also be viewed as a sandwich that the Mo atom is between the X atom and the B atom. The structural parameters, buckling height and bond length of MoXB2 are given in Table 1. Because of the large radius of Se atom, the bond length of Mo-Se (2.51 Å) is longer than that of Mo-S (2.40 Å), and the Mo–C0/B bond lengths (2.399 and 2.398 Å, respectively) in MoXB2 are similar to the Mo–C0/B bond (2.42 Å) in MoB2 monolayer [34]. The bond length of B-B are 1.75, 1.77 Å in MoXB2, which are about the same as in the TiB2 (1.79 Å) [35]. It indicates that the binding ability of bonds are strong in the MoXB2.

To confirm the structural stability, we calculated the cohesive energy $E_{coh} = (E_{Mo} + E_{X} + 2E_{B} - E_{MoXB2})/4$, where $E_{Mo}$, $E_{X}$, $E_{B}$ and $E_{MoXB2}$ are the total energies of a single Mo atom, individual X atom, an isolated B atom and one unit-cell of the MoXB2 monolayers, respectively. The calculated values are 6.62 eV per atom, 6.42 eV per atom, respectively, which are larger than the FeB2 monolayer (4.87 eV/atom) [36]. The large cohesive energy suggests that the MoXB2 monolayers are strongly bond network.

The dynamic stability of the MoXB2 (X=S, Se) monolayers are analyzed by calculating the phonon dispersion. Their phonon spectrum along the path $\Gamma(0, 0, 0) \rightarrow K(\frac{2\pi}{a}, -\frac{1}{3}, 0) \rightarrow M(\frac{2\pi}{a}, 0, 0) \rightarrow \Gamma$ (see Fig. 2) contains no unstable modes, showing that MoXB2 are dynamically stable. The highest frequency of the MoXB2 (X=S, Se) monolayers reach up to 824, 777 cm$^{-1}$, respectively. Even far higher than the highest frequency of 473 cm$^{-1}$ in MoS2 [37], indicative of robust Mo-B, Mo-X and B-B bonds in the MoXB2 (X=S, Se) monolayers.

To further determine the mechanical stability of the structures of MoXB2 (X=S, Se) monolayers, the investigation of mechanical properties began by examining the elastic constants. C$_{11}$, C$_{22}$, C$_{12}$, and C$_{66}$ are the components of the elastic modulus tensor. We first performed calculations for MoSB2, the results are C$_{11}$ = C$_{22}$ = 251.63 N/m, C$_{12}$ = C$_{21}$ = 38.32 N/m and C$_{66}$ = 106.65 N/m. For MoSeB2, the elastic constants are calculated to be C$_{11}$ = C$_{22}$ = 238.42 N/m, C$_{12}$ = C$_{21}$ = 34.47 N/m and C$_{66}$ = 101.97 N/m. Based on these tensor components, the isotropic 2D Young’s modulus (in-plane stiffness) can be estimated by calculating $(C_{11}^2 - C_{12}^2)/C_{11}$, which gives 245.79 and 233.44 N/m for MoSB2 and MoSeB2, respectively. Thus, the in-plane stiffness of MoXB2 are greatly enhanced compared with that of phosphorene (54 N/m) [38], while smaller than that of graphene (344.2 N/m) and h-BN (275.8 N/m) [39]. Additionally, the Poisson’s ration $v = C_{12}/C_{11} = 0.13, 0.14$ for MoSB2 and MoSeB2, respectively, which are smaller than that of graphene (0.17) and h-BN (0.22). It would only slightly shrink in the y direction when MoXB2 was stretched in the X direction. All these demonstrate that the MoXB2 monolayers have good mechanical properties and could have potential applications in ultrathin high-strength mechanical materials. Notably, the calculated elastic constants of the MoXB2 monolayers satisfy the conditions C$_{11}$C$_{22}$C$_{12}^2 > 0$ and C$_{66} > 0$, in agreement with the Born–Huang mechanical stability criteria.

![Fig. 1. The structure of MoXB2. (a) Top and (b) side views of relaxed structure.](image-url)
3.2 Electronic properties of the MoXB₂ (X=S, Se) monolayers

The band structure and projected density of states of MoXB₂ (X=S, Se) monolayers are shown in Figure 3. It is not difficult to analyze from the band structure diagram that MoXB₂ are direct band gap semiconductors. The band gaps of MoSB₂ and MoSeB₂ are 0.769, 0.441 eV, respectively. In addition, the direct band gap at the middle of the Γ-K, and the valence band is tangent to the Fermi energy level. One of the main factors that determine the electronic properties is the energy distribution of conduction band electrons and valence band electrons, the result can be expressed as a curve that the relationship between projected density of state (PDOS) and energy [3]. The curve indicates that the conduction band near the Fermi level mainly receive contributions from the d orbitals of Mo, and the valence band near the Fermi level mainly attributes the contributions to the p orbitals of B. Lack of inversion symmetry of MoXB₂ results in splitting of spin degenerate bands due to spin–orbit coupling (see Fig. 4). When the SOC effect is included, the top of the valence band of MoSB₂ has a significant decrease, and the details of energy bands near the Fermi level of MoSeB₂ have little influence.

4 Strain effect on electronic and optical properties

Analysis of the strain effect on the electronic characteristics of materials is an effective tool for designing electronic structures using 2D materials [40–42]. We applied the biaxial strain by fixing the lattice constant and input a series of acceptable values, which are smaller or larger than the optimized structures of MoXB₂. In our computation, the strain value is referred to the variation of the lattice constants under stress and is defined as $\varepsilon = (l - l_0)/l_0$, where $l_0$ and $l$ are lattice constants of the unstrained and strained, respectively [43]. The MoXB₂ are direct band gap semiconductors which valence band maximum (VBM) and conduction band minimum (CBM) are between the high-symmetry point Γ and K. Upon compressive strains from 0% to −10% (see Fig. 5), it is evident that increasing the strain value causes the band gap to decrease under...
compressive strain conditions, the CBM moves gradually to the high-symmetry point $\Gamma$, and the CBM moves down linearly. Moreover, the curvature of the band structure increases under compressive strains. Under the strain of $-6\%$, the CBM locates at the high-symmetry point $\Gamma$ which indicates the characters of the MoXB$_2$ monolayers transform from the direct band gap semiconductor to the indirect band gap semiconductor. Remarkably, semiconductor-semimetal transformation occurs in the MoSB$_2$ monolayer upon the strain of $-10\%$, which appears the electron-hole compensation similar to MoTeB$_2$ monolayer [44]. Meanwhile, under the strain of $-8\%$, the CBM and VBM approach and cross the Fermi surface, which also lead to the characters transformation of MoSeB$_2$ from semiconductor to semimetal.

In contrast, in the case of the tensile strain, it indicates from Figure 6 that the band gap of MoXB$_2$ increase firstly and then decrease with the increase of tensile strains, while they are still direct band gap semiconductors below the strain of $8\%$. Meanwhile, under the strain of $12\%$, MoSeB$_2$ remains direct band gap as before. Different from compression strain, in the case of the tensile strain, not only the top of valence band will move to the point of high symmetry, but also the bottom of conduction band will move to the same point of high symmetry with the increase of strain. Furthermore, VBM keeps tangent to the Fermi energy level under the limited strain (see Fig. 7).

We next investigated the optical spectra (the parallel polarization light along the a-axis) of the MoXB$_2$ monolayers under the biaxial strain. As is known, the
basic optical characteristics of materials are expressed by the dielectric function, which is a complex function and defined by \( \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \). For analyzing the complex optical characteristics of the considered material, the Kramer–Kronig transforms allows us to determine the real part of the optical dielectric function by the help of its imaginary part that can be obtained by the sum of the filled–unfilled transitions [45]. All the other parameters of the optical spectra can be derived from the dielectric function, such as absorption, reflectivity, refractive index, and energy loss function. The reflectivity coefficient can be defined as follows:

\[
\mathcal{R}(\omega) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}
\]

where \( n \) and \( k \) are the complex refractive index, they are derived by

\[
n(\omega) = \sqrt{\frac{(\epsilon_1^2 + \epsilon_2^2 + \epsilon_1}{2}
\]

\[
k(\omega) = \sqrt{\frac{(\epsilon_1^2 + \epsilon_2^2 - \epsilon_1}{2}
\]

The absorption coefficient \( \alpha(\omega) \) is obtained in terms of the real and imaginary parts of the complex dielectric function as follows:

\[
\alpha(\omega) = \sqrt{2\omega} \left[ \left( \epsilon_1^2 + \epsilon_2^2 \right) - \epsilon_1 \right]^{1/2}
\]

Here, the corresponding diagrams for the MoXB\(_2\) monolayers under the presence of the biaxial strain are illustrated in Figure 8. The optical absorption coefficients of the MoXB\(_2\) monolayers are activated at the incoming energy of about 0.38, 0.70 eV, respectively, which are close to the value of their direct band gap. From the detailed view of Figure 7, a blue shift can be found in the absorption spectrum with the increase of the biaxial compressive strain, while in the reflectivity spectrum, a blue shift occurs with the raise of the biaxial tensile strain. Moreover, MoXB\(_2\) monolayers exhibit high absorption and reflectivity in the visible region of the electromagnetic spectrum. These optical behaviors suggest that the MoXB\(_2\) monolayers have potential applications in optical devices.

5 Conclusions

In summary, we designed two kinds of Janus monolayers: MoSB\(_2\) and MoSeB\(_2\), and systematically examined their geometric structure, stability, electronic properties, optical properties and the strain effect by using a first-principles calculation in the framework of DFT. According to the calculations, the MoXB\(_2\) monolayers have excellent dynamic and mechanical stabilities that proved by phonon mode analysis and mechanical properties calculations. Investigation illustrated that the electronic and optical properties of the MoXB\(_2\) monolayers are sensitive to the biaxial strain. And the direct band gap semiconductor-indirect band gap semiconductor-semimetal transitions occurs when the biaxial compressive strain is applied. Also, the optical absorption and reflectivity of the MoXB\(_2\) monolayers exhibit a blue shift under the biaxial compressive strain or the biaxial tensile strain. Therefore, the MoXB\(_2\) monolayers may be suitable candidate materials for designing nano optoelectronic devices.
Author contribution statement

All authors analyzed and discussed the results, and contributed to the final manuscript. Qingwen Lan carried out the search for structure and property calculation, and completed the preparation of the paper. Changpeng Chen provided research direction and proofread the paper. Tian Qin discussed the method of property calculation.

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