The large absorption coefficient and photoconductivity of oP12-FeB₂ high hard material: A first-principles study

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Abstract: The structural, electronic and optical properties of the high hard structure oP12-FeB₂ have been investigated. The geometrical and electronic properties are calculated by using density functional theory (DFT) and the projector-augmented wave pseudo-potentials. The calculations of the band energy structure and the optical properties are accurately carried out by using Bethe-Salpeter equation (BSE) based on the Green's Function calculations. The absorption, reflectivity, refractivity, and photoconductivity are determined. The results with GW+BSE methods indicate that the optical properties demonstrate several novel characteristics, providing a theoretical reference for high hard semiconductor oP12-FeB₂ as a potential optical material. The mechanism of novel optical properties is explored with the density of states based on GGA+PBE calculations.

Keywords: optical properties, high hard, solar energy harvest, infrared light switch.

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1. Introduction

Metal borides have a series of advantages, especially in high hardness, excellent chemical and thermal stabilities, high melting point, neutron absorption and so on, [1] so metal borides have been widely used in many fields. Transition metals usually have high valence electron density, on the other hand, because of the small atomic radius and the strong electronegativity, boron atoms possess strong covalent bonds, the materials in which atoms combined by covalent bond possess high mechanical hardness. Over the past few decades, scientists have studied many transition metal borides in detail, such as OsB₂, [2] ReB₂, [2,3] WB₂, [4] TeB₂ [5] and so on. Recently, Kolmogorov *et al.* [6] identify an unknown structure oP12-FeB₂ by using an advanced compound prediction methods. By analyzing the thermodynamic factors, they find that oP12-FeB₂ is stabilized under pressure. [7] In previous studies, researchers have paid much attention to the mechanical properties of high hard materials. Li *et al.* [8] calculated the thermodynamic properties of FeB₂ in 2014. Wang *et al.* [9] calculate the Vickers hardness (H_v) of the oP12-FeB₂ by first-principles calculations, which confirms that the oP12-FeB₂ has reached the super hard standard ($H_v > 40$ GPa). Gou *et al.* [7] however, have demonstrated by the first principles calculations that the oP12-FeB₂ is a high hardness material with a value of 32.1 GPa. In addition, they have obtained the band structure and the density of states but not explored the optical properties.

In the frame of density functional theory (DFT), the local density approximation (LDA) and generalized gradient approximation (GGA) can give a good result for the

ground state wave function. However, DFT is a ground state theory, and it has serious shortcomings in providing a quantitative description of excited state properties. In consideration of multi-electron excited states, unfortunately, DFT usually underestimates to the extent of 30%-50% or even up to 100% for the energy band gap of the semiconductor. At the same time, the optical properties are also not accurate because the imprecise band structure. Understanding spectroscopic experiments requires the computation of excited state properties, which present a greater challenge than the ground state calculations. Based on quasi-particles concept, Green function (GW) has been applied with success to a wide variety of materials [10-14] and is better than GGA or LDA in the calculation of band structure. Despite all this, the GW method is often insufficient for describing the excitonic electron-hole interactions to calculate the optical properties. It is confirmed that Bethe Salpeter equation (BSE) [15] based on GW calculation is the best way to perform the calculation of the optical properties. [16-18]

To fill in the gap in the investigation on the optical properties of oP12-FeB₂, we carry out calculations of the optical properties by BSE based on GW calculation (GW+BSE). We use GW approximation method to carry out our calculation on the band structure of oP12-FeB₂. The optical properties of the oP12-FeB₂ structure, including absorption coefficient, refractivity, photoconductivity and so on, are calculated with GW+BSE method. The results show that the oP12-FeB₂ holds not only high hard feature but also novel optical properties.

2. Computational models and methods

The initial structure of the oP12-FeB₂ high hard material is taken from Kolmogorov *et al.* [6] and re-optimized at the GGA+PBE theoretical level. All the calculation are implemented in the Vienna ab initio simulation package (VASP) [19] and projector augmented wave [20] (PAW) method. The outer valence electrons calculated in the pseudo potential are $2s^2 2p^1$ for B atoms and $d^7 s^1$ for Fe atoms. On the technical details, the cutoff energy used for the plane wave basis set is 500.0 eV to ensure convergence for the energy calculations, in order to ensure uniform sampling in the whole Brillouin zone, according to the lattice parameters of oP12-FeB₂, Monkhorst-Pack k meshes are carefully chosen to achieve the convergence. The grids of 9×9×9 for GGA +PBE and 3×3×3 for GW+BSE are employed. The convergence of the total energy is 1×10^{-5} eV and the ion interatomic forces converge to 0.0001 eV/Å.

In the linear response range, the optical properties can be deduced by the complex dielectric function of which consists of real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$, in which the $\varepsilon_2(\omega)$ is related with the electronic absorption of material and can be derived from the momentum matrix elements of occupied and unoccupied state wave functions using proper selection rules and the $\varepsilon_1(\omega)$ can be derived from $\varepsilon_2(\omega)$ based on Kramers-Krönig transformation. The absorption coefficient, reflectivity, refractive index and photoconductivity can be derived from the complex dielectric function of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. [21]

3. Result and discussion

3.1 The structure parameters, band structure

Fig. 1 shows the models of oP12-FeB₂ structure. The primitive cell of oP12-FeB₂

structure including a total of 12 atoms, is the orthorhombic $pnma$ symmetry. There are two non-equivalent atom positions in the crystal, in which B atoms hold $8d$ (0.16211, 0.06884, 0.39193) position and Fe atoms occupy one $4c$ (0.02019, 0.25000, 0.87541) position. Because of lack of experimental data, we can only compare our parameters with the theoretical values in the literature. The present lattice parameters of oP12-FeB₂ are $a=4.780$ Å, $b=4.778$ Å, and $c=3.710$ Å, which approach to the theoretical $a=4.772$ Å, $b=4.775$ Å, and $c=3.698$ Å calculated by Gou *et al.* [7] with GGA+PBE. The calculated band structures of oP12-FeB₂ based on the GW methods are presented in Fig. 2. We can see that oP12-FeB₂ is an indirect semiconductor, and the energy band gap (E_g) is 1.25 eV with GW (Fig. 2) while the 0.65 eV of E_g given by Gou *et al.* It implies that GGA+PBE do underestimate considerably E_g of oP12-FeB₂.

3.2 Dielectric functions and electronic properties

The dielectric function is important and calculated firstly because all the optical properties can be derived from the complex dielectric function. The GW+BSE method is used to obtain the reliable complex dielectric function. The result is shown in the Fig. 3. The peaks of imaginary part in the complex dielectric functions can be understood through the electronic properties of oP12-FeB₂. The total density of states (DOS) and projected density of states (PDOS) in Fig. 4 can be used to understand the characteristic of ϵ_2 . Generally, the important peaks and valleys on the curves of ϵ_2 with BSE methods correspond to those of the contour of DOS. For example, the total DOS in Fig. 4 demonstrates that the most obvious peak of ϵ_2 near 1.5 eV is from the transition between the peak of the valence band (VB) at -0.4 eV and the twin peaks of

the conduction band (CB) around 0.9 eV. The energy positions corresponding to the dielectric function peaks are little different from those of the DOS peaks because the DOS is calculated by GGA+PBE methods. Therefore, it is acceptable to believe that the GW+BSE method can really give an exact description of the excitonic interactions. Therefore, the energies of the peak with GGA+PBE methods are undersized to compare with those of dielectric function peaks with GW+BSE methods. As shown in Fig. 4, the PDOSs of both Fe and B show similar shapes, indicating the strong hybridization between the Fe 3d and B 2p orbitals in the electronic structure of oP12-FeB₂. However, the density of Fe 3d orbitals is much stronger than that of B 2p orbitals. As a result, the transition mainly occurs between the occupation and vacancy Fe 3d orbitals. The total DOS of Fe 3d orbitals in CB keeps large from 0.9 eV to 1.4 eV, and relative large to 3.0 eV. Therefore, the imaginary dielectric function ϵ_2 demonstrates a higher peak at about 1.5 eV and a lower terrace in the whole consideration energy range.

3.3 Optical properties

The optical properties of oP12-FeB₂ are calculated with the imaginary dielectric function with GW+BSE method. The calculated optical absorption coefficient is shown in Fig. 5. A weak absorption occurs in the infrared region below 1.0 eV (above 1240 nm). The absorption coefficient rapidly increases to 1.2×10^5 /cm in the range from 1.0 eV to 1.5 eV and keep the large absorption coefficient in all range of the visible light. This characteristic indicates that oP12-FeB₂ can be used to harvest solar energy. The optical properties can be understood from the PDOS in Fig. 4. The clear absorption

peak at about 1.5 eV comes from the peak of ε_2 near 1.4 eV (the energy in the formula bring about the small shift of the position). In the entire visible region from 1.6 eV to 3.2 eV, the absorption keeps a high level, which is brought about by the terrace of ε_2 . In one word, the PDOS of Fe 3d orbitals is main responsible for the large imaginary dielectric function ε_2 from infrared to ultraviolet energy range, and then the large ε_2 results in the strong absorption in the corresponding range. Moreover, the much strong absorption in the ultraviolet energy range implies that oP12-FeB₂ can also be used as a coating material to prevent the ultraviolet light.

With both the real and imaginary dielectric functions, the reflectivity is calculated and presented in Fig. 6. The reflectivity is 0.2-0.7 in the range from infrared to ultraviolet light. In addition, it is 0.3-0.5 in the range of the visible light, which implies that oP12-FeB₂ has no strong reflectivity in the range. The complex refractive index is one of the important optical constants. The real component part n represents the refraction index which determines the propagation velocity of the light wave in the medium, and the imaginary component part k is the extinction coefficient which determines the attenuation when a light wave travels in the medium. Both the n and the k are presented in Fig. 7. The figure shows that the n is larger in the lower energy range and the maximum value reaches 8.2 at 1.4 eV. In the visible light, the n is about 3.0, which implies that oP12-FeB₂ is a high refractive material.

Photoconductivity describes the carrier mobility when materials absorb photon energy, thus increasing carrier concentration can enhance conductivity. We calculate the photoconductivity of oP12-FeB₂ and presented the results in Fig. 8. Comparing Fig.

8 with Fig. 5 and 7, the inter-band transition is relevant to carrier movement, so we find that the change of conductivity is similar to the variation of absorption or extinction coefficient k . In the infrared region, especially under 1.0 eV, the conductivity is negligibly small, but when the photon energy exceeds 1.0 eV, the conductivity increases significantly and reaches the first conductance peak of 11.1 1/fs at about 1.5 eV, which corresponds exactly to the absorption peak at 1.5 eV. The photoconductivity can well respond to the infrared light, which implies that oP12-FeB₂ should be a potential infrared light-switch material. Conductivity exceeds 2.5 1/fs in the visible light and ultraviolet region, thus oP12-FeB₂ also is a photoconductive material.

4. Conclusions

In summary, the structure optimization of the high hard oP12-FeB₂ material is investigated with GGA+PBE, while the band structure and optical properties are calculated with GW and GW+BSE, respectively. The band gap is 1.25 eV with GW but just 0.65 eV with GGA+PBE, implicating the GW calculations can remedy the seriously underestimated band gap by GGA+PBE. The optical properties with GW+BSE methods demonstrate that oP12-FeB₂ could be potential efficiency optical absorption material in the range of the visible light and the very obvious photoconductivity in the infrared range support it becomes a potential infrared light switch material. The multiple properties with the high hardness, the large absorption and the small reflection in the range of the ultraviolet region, implicating oP12-FeB₂ could be a potential ultraviolet protective material. The varied optical properties and high hard mechanical properties make oP12-FeB₂ become a promising novel material

in the photoelectronic field.

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Fig. 1. Model of oP12-FeB₂. The red and blue spheres denote the iron and boron atoms, respectively, and the black dashed lines show their primitive cells.

Fig. 2. Band structure of oP12-FeB₂ with GW.

Fig. 3. Dielectric function with BSE. ϵ_1 and ϵ_2 represent the real and imaginary part, respectively.

Fig. 4. Total and projected density of states for oP12-FeB₂.

Fig. 5. Absorption coefficient with BSE.

Fig. 6. Reflectivity with BSE.

Fig. 7. Refractive index with BSE. n and k represent the real and imaginary part, respectively.

Fig. 8. Photoconductivity with BSE.