Theoretical Study of Native Defects and Positron Annihilation States in BiOBr

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In this work, we calculated the electronic properties and formation energies of various defects in BiOBr using first principles calculations based on density functional theory. The calculated formation energies of Bi, O and Br vacancies are 9.85 eV, 3.66 eV and 1.9 eV, respectively, which suggests that the Br vacancy has the highest formation probability. We also calculated the positron trapping states of BiOBr in the perfect bulk state and vacancy trapping state. The positron bulk lifetime in BiOBr crystal is 221 ps, and the positron wave function is distributed in the layer gap. Positrons are insensitive to O vacancies, with lifetime the same as the bulk lifetime, and the positron wave function is delocalized and distributed in the layer gap region. However, the positron lifetimes in Bi and Br vacancies are 234 ps and 265 ps, respectively, and the positron wave function is localized at vacancy sites.

1. Introduction

Due to their special physical and chemical properties, photocatalytic materials show promise in many areas including energy production and reduction of environmental pollution. The ternary oxide semiconductor BiOBr has attracted attention due to its characteristic hierarchical structures, high photocatalytic activity and stability [1–4]. BiOBr has been widely applied in photocatalysis because of its increased catalytic activity and chemical stability when exposed to visible light [5,6]. It was suggested that native vacancies such as oxygen vacancies can be favorable for some photocatalytic reactions, since they can trap electrons or holes to inhibit charge carrier recombination [7]. In order to determine the most stable defect type at various experimental conditions and explore the impact of native defects on the catalytic properties, it is meaningful to evaluate the vacancy formation energies and electronic properties.

Positron annihilation spectroscopy (PAS) is a sensitive probe of vacancy-type defects in materials and positron annihilation lifetime can be measured to characterize the different type of vacancies. However, in compounds like BiOBr, the identification of vacancies by PAS is not so easy, since positrons can be trapped by various vacancy defects such as \( V_O \), \( V_{Bi} \), \( V_{Br} \) or even divacancies and vacancy clusters. In order to identify these defects, the specific positron lifetime corresponding to different defects should be obtained through theoretical calculation. In this paper, we used the atomic superposition (ATSUP) method [8] in two-component density functional theory (TCDFT) [9] for the calculation of positron states in perfect BiOBr bulk and in various defects.

2. Computational methods

2.1 Calculation of electronic properties and formation energy of defects

We used the Vienna Ab-initio Simulation Package (VASP) [10] based on the projector augmented wave (PAW) formalism of density functional theory to calculate the electronic properties and forma-
tion energies of the vacancy defects in BiOBr. The Perdew-Burke-Ernzerhof (PBE) functional [11] within the generalized gradient approximation (GGA) was used to model the exchange-correlation interactions. The electron wave function is expanded in plane waves to a cutoff energy of 400 eV which has been proved to be sufficient to give a converged result. A $4 \times 4 \times 2$ Monkhorst-Pack k-point mesh was employed to calculate the electronic properties and formation energies. The lattice parameters and atomic positions were fully relaxed using a conjugate gradient algorithm with a Hellman-Feynman force of 0.02 eV Å$^{-1}$, and electronic iterations convergence was set to $1 \times 10^{-5}$ eV. BiOBr has a layered geometrical structure, and the same atoms are on the same plane. The optimized lattice parameters of bulk BiOBr are $a = 3.93$ Å, $b = 3.93$ Å, and $c = 8.21$ Å. In order to minimize spurious defect-defect interactions, a $2 \times 2 \times 2$ supercell consisting of 16 Bi, 16 O and 16 Br atoms was constructed.

The formation energy $E_f$, is calculated using the following equation:

$$E_f = E_{\text{Defect}} - E_{\text{Bulk}} - \Delta n(Bi) \mu(Bi) - \Delta n(O) \mu(O) - \Delta n(\text{Br}) \mu(\text{Br})$$

where $E_{\text{Defect}}$ and $E_{\text{Bulk}}$ represent the total energies of the super-cell with and without a defect, respectively. $\mu(Bi)$, $\mu(O)$, and $\mu(\text{Br})$ is the chemical potential of the Bi (O, Br) element and $\Delta n(Bi)$, $\Delta n(O)$, and $\Delta n(\text{Br})$ is the number of Bi (O, Br) atoms added to ($\Delta n > 0$) or removed from ($\Delta n < 0$) the perfect supercell, respectively. The bulk BiOBr system is in equilibrium, which implies the following relationship between the chemical potentials of the Bi, O and Br elements:

$$\mu(BiOBr) = \mu(Bi) + \mu(O) + \mu(\text{Br}) = \mu_0(Bi) + \mu_0(O) + \mu_0(\text{Br}) + \Delta H_f(BiOBr)$$

where $\mu(BiOBr)$ and $\Delta H_f(BiOBr)$ are the chemical potential and the enthalpy of formation of one formula unit of BiOBr, respectively. $\mu_0(Bi)$, $\mu_0(O)$ and $\mu_0(\text{Br})$ represent the reference chemical potential of Bi, O and Br bulk. From Eq. (2), we can obtain the expression as a function of $\Delta \mu(Bi) = \mu(Bi) - \mu_0(Bi)$, $\Delta \mu(O) = \mu(O) - \mu_0(O)$, and $\Delta \mu(\text{Br}) = \mu(\text{Br}) - \mu_0(\text{Br})$ for formation energy. According to a conventional approximation, the formation energy $\mu(Bi) = \mu_0(Bi) (\mu(O) = \mu_0(O)$, $\mu(\text{Br}) = \mu_0(\text{Br})$) while under Bi-rich (O-rich, Br-rich) condition.

### 2.2 Calculation of positron-annihilation

Positron-annihilation calculations are performed using the atomic superposition (ATSUP) method, which is an efficient method for modeling positron states and annihilation in solids. The positron-annihilation lifetime depends on the positron annihilation rate which can be calculated from the overlap integral as:

$$\frac{1}{\tau} = \lambda = \pi r_0^2 c \int dr n^+(r)n^-(r)g(0; n^+; n^-)$$

where $r_0$ is the classical electron radius, $c$ is the speed of light, $n^+(r)$ and $n^-(r)$ are the positron and electron density, and the $g(0; n^+; n^-)$ term is the electron-positron pair correlation functional which is called the enhancement factor of the electron density at the positron annihilation site. In order to obtain the positron $n^+(r)$ and electron $n^-(r)$ densities in our calculations, a non-self-consistent electron density and coulomb potential is considered to be within each isolated atom electron density and coulomb potential superposition [12]. In the non-self-consistent steps, we used the conventional scheme of the two-component density-functional theory (TCDFT). For the above scheme, we chose the local density approximation and the well-established Boronski-Nieminen parametrization to calculate the positron-electron correlation potential as well as the enhancement factor of positron annihilation [13].
3. Results and discussion

3.1 Electronic properties

We performed detailed calculations of the band structures and ‘density of states’ (DOS) for a series of defects. The vacancy-type defects included vacancies of the Bi, O and Br lattices. In addition, we also analyzed the band structure and DOS of the BiOBr crystal and compared the results.

Figure 1 presents the band structures and DOS in the BiOBr crystal. The band structure and the DOS show a correspondence to each other. The calculated band gap value of BiOBr is 2.27 eV. It is obvious that BiOBr is an indirect band gap semiconductor, and the Fermi level is close to the top of the valence band. Through the comparative analysis of ‘partial density of states’ (PDOS) it can be found that the top of the valence band is mainly composed of p orbital electrons of O and Br atoms, and at the bottom of the conduction band is mainly composed of d orbital electrons of Bi atom.

Figures 2–4 present the band structures and DOS of Bi, O and Br vacancy defects, respectively. The band gaps of Bi, O and Br vacancy defects are 1.98 eV, 0.99 eV and 2.10 eV, respectively, which are all smaller than the band gap in the BiOBr crystal. This can be explained by the DOS. For the Bi vacancy (Fig. 2), the existence of defects leads to the emergence of hybrid energy levels, the top of valence band crosses the Fermi level and the band gap value decreases. At the top of the

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Fig. 1 The band structure (left) and Density of States (right) of the BiOBr crystal.

Fig. 2 The band structure (left) and Density of States (right) of the Bi vacancy.
valence band, it is mainly contributed by p orbital electrons of O and Br atoms. At the bottom of the conduction band, it is mainly contributed by p orbital electrons of Bi. For the O vacancy (Fig. 3), a new independent hybrid energy level appears near the top of valence band and the band gap value decreases. For the Br vacancy (Fig. 4), the bottom of the conduction band crosses the Fermi level and the band gap value decreases. In conclusion, the existence of vacancy defects leads to the occurrence of hybrid energy levels, which affects the structural and electronic properties of the crystals.

Table 1  Calculated formation energies of different vacancy defects (neutral charge state) in BiOBr.

<table>
<thead>
<tr>
<th>Defects</th>
<th>$V_{\text{Bi}}$</th>
<th>$V_{\text{O}}$</th>
<th>$V_{\text{Br}}$</th>
<th>$V_{\text{BiO}}$</th>
<th>$V_{\text{BiO}}$</th>
<th>$V_{\text{Br}}$</th>
<th>$V_{\text{BiOBr}}$</th>
</tr>
</thead>
</table>
3.2 Formation energy of defects
In this paper, the formation energies for various vacancy defects were calculated. The vacancy-type defects include vacancy of Bi, O and Br lattices (labelled as $V_{\text{Bi}}$, $V_{\text{O}}$ and $V_{\text{Br}}$), and also some divacancies (labelled as $V_{\text{BiO}}$, $V_{\text{BrO}}$ and $V_{\text{BiBr}}$) and vacancy clusters (labelled as $V_{\text{BiOBr}}$). Only the neutral charge state is considered for all these vacancies. The calculated results are listed in Table I. For monovacancies, divacancies and vacancy clusters, $V_{\text{Br}}$ has the lowest formation energy. This indicates that the Br vacancy defect has the highest formation probability among these vacancies.

3.3 Positron-annihilation states
Positron annihilation lifetimes and positron wave functions at various neutral vacancy defects in BiOBr were also calculated. The positron annihilation lifetimes in the perfect lattice and at various defect sites are listed in Table II. The positron lifetime in the perfect BiOBr lattice is 221 ps, and that at $V_{\text{O}}$ shows no change compared with this bulk lifetime. This means that PAS cannot detect oxygen vacancies in BiOBr. This is a general trend in almost all oxides. For $V_{\text{Bi}}$ and $V_{\text{BiO}}$, the positron lifetime has a slight increase compared with the bulk lifetime, i.e. 234 ps and 239 ps, respectively. For the other vacancies, such as $V_{\text{Br}}$, $V_{\text{BiBr}}$ and vacancy clusters, the positron lifetime shows a further increase. In particular it increases to 290 ps at $V_{\text{BiOBr}}$. This suggests that $V_{\text{Br}}$, $V_{\text{BiBr}}$ and $V_{\text{BiOBr}}$ can be easily distinguished by positron lifetime measurements.

The positron wave function distributions in the perfect lattice and at various defect states are plotted in Figs. 5–6. The positron wave function is distributed in the gap of the atomic layers for a perfect BiOBr crystal. At $V_{\text{O}}$, the positron wave function shows no localization, i.e. it is almost the same as that in the perfect lattice. This explains why the positron lifetime at $V_{\text{O}}$ is the same as the bulk lifetime. For $V_{\text{Bi}}$ and $V_{\text{BiO}}$, the positron wave function is weakly localized at the defect site, and some part is still distributed in the atomic layer gap. This is the reason for the slight increase of the positron lifetime localized in $V_{\text{Bi}}$ and $V_{\text{BiO}}$ compared with the bulk lifetime. For the other vacancy defects, the positron wave function shows stronger localization, which leads to a notable increase of the positron lifetime, since the electron density is reduced at vacancy sites.

**Table II**
Calculated positron-annihilation lifetimes at different states in BiOBr.

<table>
<thead>
<tr>
<th>System</th>
<th>Perfect lattice</th>
<th>$V_{\text{Bi}}$</th>
<th>$V_{\text{O}}$</th>
<th>$V_{\text{Br}}$</th>
<th>$V_{\text{BiO}}$</th>
<th>$V_{\text{BrO}}$</th>
<th>$V_{\text{BiBr}}$</th>
<th>$V_{\text{BiOBr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positron lifetime [ps]</td>
<td>221</td>
<td>234</td>
<td>221</td>
<td>265</td>
<td>239</td>
<td>266</td>
<td>286</td>
<td>290</td>
</tr>
</tbody>
</table>

**Fig. 5** Positron wave function distribution (yellow area) in the perfect lattice and at $V_{\text{O}}$. 
4. Conclusion

In this work, the electronic properties of various defects in BiOBr were evaluated, and the formation energies of these defects were calculated. The results of the band structures and DOS show that due to the formation of hybrid energy levels, the band gap values of vacancy defects are smaller than that of the perfect BiOBr crystal. The $V_{\text{Br}}$ defect is the most easily formed with the lowest formation energy among these defects. The positron trapping and annihilation states in the perfect bulk state and vacancy trapping states were also calculated. The positron wave function is distributed in the gap of the atomic layers for a perfect BiOBr crystal, and positrons are insensitive to O vacancies. For the other defect states, the positron wave function shows strong localization at vacancy sites, which leads to an increase of the positron lifetime. It is therefore possible to discriminate these defects by careful measurements of positron lifetime in BiOBr.

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References