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First principles study of trirutile magnesium bismuth oxide: Ideal bandgap for photovoltaics, strain-mediated band-inversion and semiconductor-to-semimetal transition

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ABSTRACT

Magnesium Bismuth Oxide ($MgBi_2O_6$) has been experimentally synthesized three decades ago, however, an in-depth theoretical understanding of its electronic structure is still lacking. The bandgap of $MgBi_2O_6$ is calculated to be 1.10 eV based on Heyd – Scuseria – Ernzerhof (HSE) functional method, which is the same as that of Silicon. Moreover, the bandgap can be widely tuned by the external strain and leading to a semiconductor-to-semimetal transition with a Dirac-like band crossing. Our tight-binding (TB) model can well reproduce the electronic structure of $MgBi_2O_6$ in the presence of strain. More interestingly, we also predict that strain can effectively reduce effective electron mass and enhance visible light absorption. The favourable bandgap and substantial tuning of electronic structure in $MgBi_2O_6$ will place it as a promising candidate for novel photovoltaic and optoelectronic application.

1. Introduction

Searching for new materials with suitable bandgap, excellent optical properties and high charge carrier mobility is critical to the development of innovative technologies for next generation photovoltaics, photonics and electronics. In recent years, oxides containing Bi atoms [1–7] such as $CaBi_2O_4$, $VBiO_4$, WBi_2O_6, $NaBiO_3$, $MgBi_2O_6$ have been identified as excellent visible-light-driven photocatalysts in experiments. Among them, $MgBi_2O_6$ was firstly synthesized in 1997 [8] by low-temperature hydrothermal reaction and microwave hydrothermal processing methods [9]. The tetragonal lattice parameters were identified to be a = b = 4.826 Å and c = 9.719 Å. From UV–vis spectra [5] and X-ray diffraction patterns [10] experimental estimation, the bandgap energies for the $MgBi_2O_6$ film are 1.6 eV and 1.8 eV respectively, which are close to the ideal bandgap for photovoltaics application. Theoretically, a previous study predicted a bandgap of 0.8 eV using the linear muffin-tin orbital (LMTO) method [11], whereas another first principles investigation claimed that it is metallic resulting from the overlapping of valence bands (VB) and conduction band (CB) [12]. Clearly, there is an urgent need for a careful re-examination of the physical and electronic properties of trirutile $MgBi_2O_6$ due to the discrepancy between experimental and computational studies.

Generally, a high switch on-off ratio tunable bandgap [13] and a dispersive CB [14] are highly desirable for an effective optoelectronic material. In $MgBi_2O_6$, previous experimental study revealed that the optical absorption peak is ascribed to the charge transfer between the valence band maximum (VBM) with large contribution from O-2p orbital, and the conduction band minimum (CBM), which has predominantly Bi-6s orbital character [10]. The electronic structure of the Bi^{5+} trirutile oxides shares a number of common characteristics with well-known transparent conducting oxides (TCO) materials [10]. For instance, the bandgap and work function in TCO can be substantially modulated, which indicates that it is possible to tune interaction between the Bi^{5+} 6s and O 2p orbitals. Strain engineering has recently demonstrated to be an effective and promising way to alter electronic, transport, and optical properties of semiconductors [15–19]. For examples, in-plane hopping amplitude of graphene can be changed in an anisotropic way via strain [20], a broader range of the solar spectrum can be absorbed in monolayer MoS_2 in the presence of a biaxial strain from 0% to 9% [21]. In addition, strain can mediate bandgap [15], leading to a transition from indirect to direct bandgap [22], and an improved carrier mobility [23]. Hence exploiting strain engineering the electrical properties of $MgBi_2O_6$ is of a great interest.

In this work, first-principles calculations have been performed to study the electronic and optical properties of trirutile $MgBi_2O_6$ with particular focus on the effect of external strain. The bandgap for strain-free $MgBi_2O_6$ by HSE method is calculated to be 1.1 eV, which is quite close to the experimental value. Interestingly, it is found that strain can

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not only substantially tune bandgap to a value close to the ideal bandgap for solar cell application, but also induce a semiconductor to semimetal transition for $MgBi_2O_6$. Our TB model for $MgBi_2O_6$ under strain can reproduce the DFT results and offer clear physics picture of strain engineering. Additionally, the light absorption spectra of $MgBi_2O_6$ can be also significantly tuned in the presence of strain. The absorption edges distribution expanded from approximately 500 nm (strain-free) into 800 nm with three more distinct absorption peaks, indicating a red shift and enhanced visible light absorption capability. Furthermore, electron effective mass can be reduced under tensile strains. Our results suggest that $MgBi_2O_6$ has great potential for the application in building novel optoelectronic, solar cell and electronic devices due to its modulation by external strain.

2. Computational methods

First-principles calculations were performed based on DFT using the plane wave basis VASP code [24–26]. The hybrid DFT based on the HSE exchange–correlation functional [27] was adopted for the calculation of geometries, band structures as well as the optical absorption spectrum of $MgBi_2O_6$. For comparison, the generalized gradient approximation in the Perdew, Burke, and Ernzerhof form (GGA-PBE) exchange − correlation functional [28] was also used for the calculations of band structures of $MgBi_2O_6$. The plane wave energy cut-off was set to 500 eV and the structure was fully relaxed until energy and force were converged to 10^{-6} eV and 0.01 eV/Å. The band structure of $MgBi_2O_6$ was calculated with Monkhorst k-point meshes of 0.0015 $Å^{-1}$. The electron effective mass (m^*) of the electrons at the conduction band minimum (CBM) is estimated from the curvature of the electronic band dispersion, i.e. the formula $m^* = \hbar\left(\frac{\partial E^2}{\partial k^2}\right)^{-1}$, where E and k are the band energy and reciprocal lattice vector. For anisotropic materials, $m^* = \sqrt{m_i^* m_j^* m_k^*}$ where i, j and k label the transport direction (x, y or z).

3. Results and discussions

$MgBi_2O_6$ crystallizes in the trirutile structure and possesses tetragonal crystal structure with space group P42/mnm. We calculated the lattice parameters and band structure using both the hybrid HSE06 functional (Fig. 1(c)) and the PBE functional (Fig. 1(b)) methods. The PBE method overestimates the experimental lattice constants by 2%, whereas the HSE06 can successfully reproduce the lattice parameters (a = b = 4.82 Å, c = 9.68 Å). It is well known that bandgap can be more accurately predicted for a variety of metal oxide systems by HSE06 method [29–32], we therefore focus on the discussions based on the results from HSE06 in the following. Fig. 1 presents the calculated band structure for $MgBi_2O_6$ with a HSE06 bandgap of 1.1 eV, which is close to the experimental value [5,10]. In contrast, by PBE functional method, the electronic property of $MgBi_2O_6$ is predicted to be metallic, where two bands cross each other along M-Γ-Z, as shown in Fig. 1(b) due to the well-known bandgap underestimation. This is probably the reason that the conflicting conclusions were obtained from different theoretical simulations [11,12].

Strain engineering has been demonstrated to be an efficient way to tune material's electronic properties [15,33]. It is expected that strain can modify the bond strength and modulate the energies of the conduction and valence band edges due to the wavefunction overlap, thus altering the bandgap [34]. Fig. 2(a)–(h) presented the change of band structure and gap as a function of external hydrostatic strain. Clearly, the compressive strain shifted the conduction bands to a higher energy and significantly increased bandgap, while tensile strain moved conduction band minimum to a lower energy and thus reduced the bandgap. With a moderate 2% compressive strain, the bandgap enlarges to 1.47 eV, which is very close to the ideal optical bandgap of solar cell materials (1.5 eV). At a strain of +7%, the conduction band minimum is moved to below the valance band maximum, leading to a semiconductor-to-semimetal transition. It is also worth noting that the CB of $MgBi_2O_6$ is very dispersive around the Γ point, signifying a very low electron effective mass. The effective mass of electron is calculated to be 0.277m_e (see Fig. 2(j)) and can be further reduced to 0.244m_e under a moderate strain of 5%. The small mass will greatly improve charge carrier mobility, suggesting great potential for application of $MgBi_2O_6$ in electronics and photonics. In addition, the lattice parameters and bond length of $MgBi_2O_6$ under different strain is given in Table s1.

The effect of strain on the bandgap can be understood by analysing the orbital-resolved band structures as shown in Fig. 3. The contribution to the VBM at the Γ point is dominated by the px and py orbitals of O, while the CBM at the Γ point mainly consists of the s orbital of Bi and pz orbital of O as shown in Fig. 3(a). With increasing tensile strain, the energy of the s-orbital of Bi and pz-orbital of O decrease, while the px and py orbitals shift up in energy. These results in the shift of CBM and VBM towards the Fermi level and the touch of CBM and VBM at a critical strain before their energies crossing at a higher one. When strain was further increased, those orbitals continued to shift gradually away

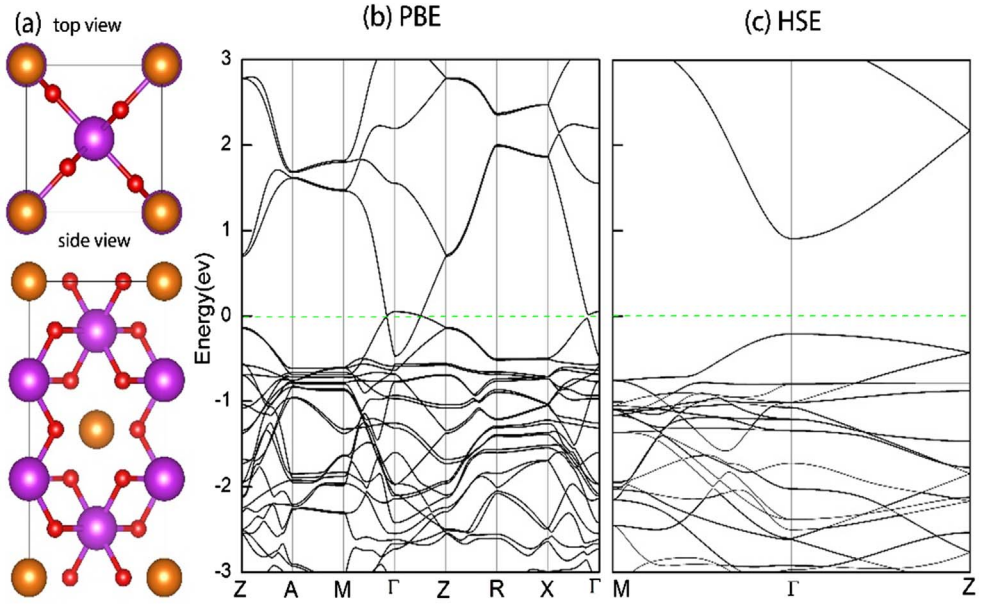

Fig. 1. (a) Top and side views of the unit cell of trirutile $MgBi_2O_6$. The purple, red and orange spheres represent Mg, O, and Bi atoms, respectively. (b) and (c) represent the band structures of $MgBi_2O_6$ calculated by PBE and HSE methods, respectively. Due to that the band states crossing near the Fermi level is along M-Γ-Z while all other bands are far away from Fermi level, the band structure from HSE calculation is shown only along M-Γ-Z. The Fermi level is indicated by the green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)