Crystal engineering of $\text{Bi}_2\text{WO}_6$ to polar

Aurivillius-phase oxyhalides

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Abstract

The Aurivillius phases of complex bismuth oxides have attracted considerable attention due to their lattice polarization (ferroelectricity) and photocatalytic activity. We report a first-principles exploration of $\text{Bi}_2\text{WO}_6$ and the replacement of $\text{W}^{6+}$ by pentavalent ($\text{Nb}^{5+}$, $\text{Ta}^{5+}$) and tetravalent ($\text{Ti}^{4+}$, $\text{Sn}^{4+}$) ions, with charge neutrality maintained by the formation of a mixed-anion oxyhalide sublattice. We find that $\text{Bi}_2\text{SnO}_4\text{F}_2$ is thermodynamically unstable, in contrast to $\text{Bi}_2\text{TaO}_5\text{F}$, $\text{Bi}_2\text{NbO}_5\text{F}$ and $\text{Bi}_2\text{TiO}_4\text{F}_2$. The electric dipoles introduced by chemical substitutions in the parent compound are found to suppress the spontaneous polarization from 61.55 $\mu\text{C/cm}^2$ to below 15.50 $\mu\text{C/cm}^2$. Analysis of the trends in electronic structure, surface structure, and ionization potentials are reported. This family of materials can be further extended with control of layer thicknesses and choice of compensating halide species.
Introduction

Metal oxides have been studied intensively for applications such as photoelectrochemistry, photocatalysis, and transparent electronics.\textsuperscript{1–4} These studies are motivated by their low cost, high stability, and wide range of physical properties.\textsuperscript{3,5,6} For photochemical and optoelectronic applications, specific band gaps and band alignments are required to optimize the device performance. Since many metal oxides have a valence band maximum (VBM) composed of O 2p orbitals, resulting the VBM levels to be within a similar range.\textsuperscript{7} Therefore, they often have difficulties in meeting the band alignment requirements. The most prominent example is when metal oxides are used as photoanodes for water splitting, where the valence band energy is too deep to efficiently support oxygen evolution reactions.\textsuperscript{5,8} For the reaction to occur efficiently, the VBM must be higher in energy (closer to vacuum) so that holes can be effectively transmitted to water. The valence band energy is relevant in other areas including p-type transparent electrodes.\textsuperscript{4,9}

Efforts to modulate the valence band energy of metal oxides include the employment of $ns^2$ post-transitional metal cations or mixed anions.\textsuperscript{10–13} There are few examples were these approaches are used in tandem, and there have been some notable successes.\textsuperscript{12} The combination of high-throughput material screening and experimental synthesis reported a p-type transparent conducting oxide Ba$_2$BiTaO$_6$, where high hole mobility was attributed to the hybridization of Bi 6s and O 2p levels.\textsuperscript{14} Other experimental work has demonstrated that compounds in Sillen-Aurivillius phase, Bi$_4$NbO$_8$X (where X=Cl, Br, I), exhibit an elevated valence band.\textsuperscript{15–17} The ability of halide anions to change the strength of O–cation bond, and hybridization of Bi with O 2p levels, combine to raise the VBM compared to conventional metal oxides.\textsuperscript{12,13} These studies suggest effectiveness of adopting mixed anion ternary and quaternary bismuth oxides to obtain elevated VBM. In particular, the chemical flexibility of Aurivillius phase compounds are expected to be suitable for this approach.\textsuperscript{18}

The general formula of the Aurivillius family is \((\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}\). Much effort has been put into studying russellite Bi$_2$WO$_6$ (m=1), a naturally occurring mineral,
which exhibits high catalytic performance and ion conductivity.\textsuperscript{22–24} However due to its chemical and structural complexity, even in the simplest case of Bi\textsubscript{2}WO\textsubscript{6}, there is still much to be explored. Early in the research of this compound, several crystal structure models were proposed.\textsuperscript{25,26} However, it is now generally accepted that Bi\textsubscript{2}WO\textsubscript{6} has polar $P2_1ab$ symmetry at low and intermediate temperatures.\textsuperscript{27–29} Above 700 °C, the structure transforms into orthorhombic $ABA2$ symmetry through a second-order phase transition.\textsuperscript{27,30,31} Further heating to about 950 °C transform the crystal to the $A2/m$ symmetry through a first-order phase transition, where the spontaneous polarization disappears ($T_C = 950^\circ$C).\textsuperscript{27,31,32} Density functional theory (DFT) calculations have been used to probe the mechanism behind the structural phase transition of Bi\textsubscript{2}WO\textsubscript{6}.\textsuperscript{31,33} Recently, researchers have expanded their scope to quaternary mixed anion compounds based on Bi\textsubscript{2}WO\textsubscript{6}, such as Bi\textsubscript{2}TaO\textsubscript{5}F, Bi\textsubscript{2}NbO\textsubscript{5}F and Bi\textsubscript{2}TiO\textsubscript{4}F\textsubscript{2} and the photocatalytic performance of these compounds were measured.\textsuperscript{34–36} These studies have shown the effectiveness of replacing the $B$-site cation and adding F to make a mixed-anion compound. Although the high potential of quaternary compounds was shown,\textsuperscript{34–41} less is known about their electronic characteristics.

In this study, we systematically expand the crystal system by replacing W\textsuperscript{6+} in Bi\textsubscript{2}WO\textsubscript{6} with pentavalent Ta\textsuperscript{5+} and Nb\textsuperscript{5+} and with tetravalent Ti\textsuperscript{4+} and Sn\textsuperscript{4+}. F\textsuperscript{−} were also incorporated to O\textsuperscript{2−} site resulting the charge neutrality to be maintained. Therefore, we have explored properties of ternary compound Bi\textsubscript{2}WO\textsubscript{6}, and quaternary compounds Bi\textsubscript{2}TaO\textsubscript{5}F, Bi\textsubscript{2}NbO\textsubscript{5}F, Bi\textsubscript{2}TiO\textsubscript{4}F\textsubscript{2} and Bi\textsubscript{2}SnO\textsubscript{4}F\textsubscript{2}, in detail using first-principles materials modelling. We report that substitution of O with F resulted in modified perovskite-like (BO\textsubscript{4})\textsuperscript{2−} layer, which suppressed the magnitude of spontaneous electric polarization. Furthermore, the quaternary compounds exhibited higher VBM compared to Bi\textsubscript{2}WO\textsubscript{6} and each of conduction band minimum levels differed largely, suggesting high tunability of the band edge energy. Together, these results demonstrate the diverse material properties of Bi\textsubscript{2}WO\textsubscript{6}-based compounds and open up a path towards developing new Bi-based mixed anion compounds.
Methods

Atomic structure models

A crystal structure model of Bi$_2$WO$_6$ was obtained by optimizing the initial (room temperature) structure determined from X-ray diffraction.

$B$-site cations, W, in Bi$_2$WO$_6$ were replaced by Nb, Ta, Ti and Sn, together with F to keep the same valence electron count, resulting in Bi$_2$TaO$_5$F, Bi$_2$NbO$_5$F, Bi$_2$TiO$_4$F$_2$ and Bi$_2$SnO$_4$F$_2$, respectively (Figure 1). Since there are degrees of freedom for the F distribution amongst the anion sites, 20 different F configurations were considered for each compound. Within the 20 configurations, 5 were chosen so that F aligned in certain crystal planes and the rest were randomly selected using the site-occupancy disorder code. To validate the dependence of F configurations, four most stable F configurations were calculated for each quaternary oxides. However, F configurations had little effect on the properties of interest, therefore, only the results of the most stable structures are presented.

To assess the thermodynamic stability of the Aurivillius phase compounds, a number of decomposition reactions were considered. When the product (secondary phases) have lower energy, the reaction is exothermic, thus suggesting the quaternary compound to be unstable over any chemical potential range.

Density functional theory calculations

DFT calculations were performed within the projector augmented wave scheme as implemented in VASP. The VESTA package was used to visualize the atomic structures. Both HSE06 and PBEsol were used for the exchange correlation functional as described below.

Structure relaxation and calculation of spontaneous polarization were performed using PBEsol, while further electronic structure and total energy analysis was performed with HSE06. A plane wave cutoff of 550 eV, $k$-point sampling of at least $5\times5\times2$ for the primitive
unit cell of 36 atoms, and electronic convergence criteria of $10^{-8}$ eV were employed. The lattice constants and the internal coordinates were optimized until the residual force became less than 1.0 meV/Å.

**Spontaneous lattice polarization**

Lattice polarization was calculated with the PBEsol functional within the Berry phase formalism.\textsuperscript{50,51} In modern theory of polarization, the spontaneous polarization $\Delta p$ is defined as follows:

$$\Delta p = P_{\text{polar}} - P_{\text{non-polar}} + n\Delta P_Q.$$  \hspace{1cm} (1)

Here, $P_{\text{polar}}$ is the polarization of the polar phase, $P_{\text{non-polar}}$ is the polarization of the non-polar phase, $n$ is an integer and $\Delta P_Q$ is a polarization quanta. This definition leaves an ambiguity in the value of spontaneous polarization $\Delta p$ with respect to modulo $\Delta P_Q$. The polarization quanta $\Delta P_Q$ in aurivillus phase compounds was smaller than the spontaneous polarization $\Delta p$ (Table 1), making it difficult to determine the exact value of spontaneous polarization $\Delta p$ from a single calculation. Therefore, ideal (fictitious) non-polar centrosymmetric parent structures were considered and the spontaneous polarization $\Delta p$ was calculated by tracing the polarization as the structure was gradually changed to the original polar $P2_1ab$ symmetry (Figure 3). Since spontaneous polarization as some dependence on F configurations in the oxyhalide systems, the four most stable F configurations were calculated for each of the quaternary compounds.

**Surface structure and stability**

To find the favored crystal terminations, the atomic chemical potentials were used to obtain the surface formation energies. First, the set of chemical potentials which stabilize Bi$_2$WO$_6$ were obtained by comparing the formation enthalpy with the competing binary oxides, WO$_2$, \hspace{1cm}
WO$_3$ and Bi$_2$O$_3$. The formation enthalpy was calculated as follows:

$$
\Delta H_f^{\text{Bi}_2\text{WO}_6} = E_{\text{Bi}_2\text{WO}_6} - 2E_{\text{Bi}} - E_{\text{W}} - 6E_{\text{O}},
$$

(2)

where $E_{\text{Bi}}$, $E_{\text{W}}$, $E_{\text{O}}$ is the energy per atom for the standard state of each elements which are Bi metal, W metal and molecular O$_2$, respectively. To stabilize the material, the chemical potential with respect to the standard states of Bi, W and O should satisfy the following inequality:

$$
\Delta H_f^{\text{Bi}_2\text{WO}_6} = \Delta \mu_{\text{Bi}_2\text{WO}_6} - 2\Delta \mu_{\text{Bi}} - \Delta \mu_{\text{W}} - 6\Delta \mu_{\text{O}}
$$

(3)

$$
\Delta \mu_{\text{Bi}} \leq 0, \Delta \mu_{\text{W}} \leq 0, \Delta \mu_{\text{O}} \leq 0.
$$

(4)

Secondly, surface formation energies $\Delta E_{\text{surf}}^f$ for given chemical potentials were calculated. Accounting for the fact that Bi$_2$WO$_6$ is likely to exhibit surfaces on the [001] direction,$^{52,53}$ five different models with (001) surface terminations were considered.

Surfaces were described using symmetric slab models with a thickness of at least 32 Å and vacuum thickness of about 20 Å. The atomic structures were relaxed with the PBEsol functional and their energies were calculated with the HSE06 functional. Then, the following equation was used to calculate the surface formation energies:

$$
\Delta E_{\text{surf}}^f = (E_{\text{surf}} - n_{\text{Bi}}\mu_{\text{Bi}} - n_{\text{W}}\mu_{\text{W}} - n_{\text{O}}\mu_{\text{O}})/2,
$$

(5)

where $E_{\text{surf}}$ is the energy of slab model calculated, and $n_i$ is number of the chemical species $i$ in the slab model. Lastly, from the most stable surface structure of Bi$_2$WO$_6$, surfaces for the quaternary oxides were made and the band edges of bulk were aligned by using the vacuum level as a reference using the MacroDensity package.$^{54}$
Results

Crystal structure

Bi$_2$WO$_6$ consists of fluorite-like (Bi$_2$O$_2$)$^{2+}$ layers and perovskite-like (WO$_4$)$^{2-}$ layers as shown in Figure 1. Early studies of Bi$_2$WO$_6$ reported a range of structure types including $I4/mmm$,$^{25}$ $B2cb$,$^{26}$ and $P2_1ab$ (referred as $Pca2_1$).$^{24,42}$ There is growing consensus that this material exhibits the $P2_1ab$ structure around room temperature.$^{27,30–32}$ Our optimized structural parameters, listed in Table 1, are in good agreement with experimental results, which have reported the lattice constants of Bi$_2$WO$_6$ to be 5.45 Å, 5.43 Å, 16.40 Å (converted from $Pca2_1$ setting).$^{27}$

For quaternary compounds, the most stable F ion configurations within 20 calculated structures are presented in Figure 1. All of the structures were orthorhombic with the lattice constants shown in Table 1. With the exception of Bi$_2$SnO$_4$F$_2$, the volume of the unit cell decreased as the $B$-site cation decreased its valence (Table 1). The length of each axis depends on the F configurations and the trends can be explained by the $B$-site cation and F ($B$–F) bond length. The $B$–F bond length is longer than $B$–O, which causes the octahedra to be elongated in the F direction. This elongation causes the volume of the octahedra to decrease and resulted the $B$-ion to move closer to the center of the octahedra. Overall, in quaternary compounds, substitution of O by F ions largely changed the local structure of the perovskite-like (BO$_4$)$^{2-}$ layer.

The thermodynamic stability of the compounds were assessed by whether a material will decompose to its competitive phases. All compounds were found to be stable (see Supporting Information) with the exception of Bi$_2$SnO$_4$F$_2$. The following decomposition reaction of the Bi$_2$SnO$_4$F$_2$ is exothermic:

$$\Delta H = 2E_{\text{Bi}_2\text{SnO}_4\text{F}_2} - E_{\text{Sn}_2\text{Bi}_2\text{O}_7} - E_{\text{BiOF}} - E_{\text{BiF}_3} = 1.11 \text{ eV.}$$ (6)
In this process, the enthalpy change $\Delta H$ was 1.11 eV, suggesting trio of Sn$_2$Bi$_2$O$_7$, BiOF and BiF$_3$ to be preferred over Bi$_2$SnO$_4$F$_2$ at any chemical potential range. Since Bi$_2$SnO$_4$F$_2$ was unstable, hereafter, we will focus on four compounds, Bi$_2$WO$_6$, Bi$_2$TaO$_5$F, Bi$_2$NbO$_5$F and Bi$_2$TiO$_4$F$_2$.

Table 1: Structure, polarization quanta ($\Delta P_Q$) and spontaneous polarization ($\Delta p$) of Aurivillius phase oxides.

| Compound | $a$ (Å) | $b$ (Å) | $c$ (Å) | volume (Å$^3$) | $\Delta P_Q$ ($\mu$C/cm$^2$) | $\Delta p$ ($\mu$C/cm$^2$) |
|----------|---------|---------|---------|----------------|-----------------------------|-----------------------------|
| Bi$_2$WO$_6$ | 5.44    | 5.44    | 16.55   | 489.66         | 17.79                       | 61.55                       |
| Bi$_2$TaO$_5$F | 5.40    | 5.41    | 16.58   | 484.26         | 17.87                       | 10.68                       |
| Bi$_2$NbO$_5$F | 5.39    | 5.40    | 16.58   | 482.08         | 17.90                       | 15.50                       |
| Bi$_2$TiO$_4$F$_2$ | 5.36    | 5.38    | 16.30   | 470.15         | 18.26                       | 15.15                       |
| Bi$_2$SnO$_4$F$_2$ | 5.53    | 5.53    | 16.83   | 515.02         |                             |                             |

**Electronic structure**

The atom-projected electronic density of states were used to investigate the contribution of each element to upper valence band and lower conduction band, as shown in Figure 2. Six inequivalent O-sites in this crystal structure were grouped according to the nearest cation. For example, in Bi$_2$WO$_6$, 16 O atoms were labeled O$_{Bi}$ and eight of them were labeled O$_{W}$ as shown in Figure 2. It should be noted that for quaternary compounds, the number of O atoms near Bi and O atoms near B-site cation varies according to the F configurations.

All four compounds, Bi$_2$WO$_6$, Bi$_2$TaO$_5$F, Bi$_2$NbO$_5$F and Bi$_2$TiO$_4$F$_2$, are insulators with band gaps of 2.88, 4.16, 3.56 and 3.93 eV, respectively. Experimental studies reported that Bi$_2$WO$_6$ has band gap of 2.8 eV, in good agreement with our calculation.$^{22,52,55}$ Judging from the small lattice constant differences, the slight overestimate of the band gap is likely to originate from the choice of the HSE06 exchange correlation functional. For the quaternary compounds, experimental studies have reported the band gaps of Bi$_2$TaO$_5$F, Bi$_2$NbO$_5$F and Bi$_2$TiO$_4$F$_2$ to be 2.86, 2.95, and $\sim$3.06 eV, respectively.$^{34,36,41}$

In addition to the band gap overestimation arising from the HSE06 functional, the smaller measured band gaps are likely to be influenced by point and extended defects. Both experi-
mental and theoretical works reported that in Bi$_2$WO$_6$, oxygen vacancies are easily formed and contribute to band gap narrowing.$^{53,56-58}$ Similar characteristics are expected for quaternary compounds. Since the experimental measurements of Bi$_2$TaO$_5$F, Bi$_2$NbO$_5$F and Bi$_2$TiO$_4$F$_2$ were performed for porous structures, abundance of defects are likely to be the reason for the smaller band gaps to be observed.

In each of the compounds studied, the upper VB is mainly composed of the anti-bonding state of the O $p$ orbitals with hybridization with the Bi $s$ orbitals (−1.0–0.0 eV in Figure 2). The narrow band width indicates the localized nature of these bands. The density of states for Bi$_2$WO$_6$ is in good agreement with the previous studies.$^{31,57,59}$ In the quaternary compounds, the F levels fall deeper into the valence band (≈ −1.0 eV in Figure 2). This is in contrast in the case of PbBiO$_2$I, where the upper VB is mainly composed of I 5$p$ levels. This energy level resulted the oxidation of I to be favored over water, causing the ratio of I to decrease during oxidation reactions.$^{13}$ Therefore, having F 2$p$ deeper into the valence band is a favorable property in a perspective of avoiding photocatalyst degradation.

The lower conduction band of Bi$_2$WO$_6$, Bi$_2$TaO$_5$F, Bi$_2$NbO$_5$F and Bi$_2$TiO$_4$F$_2$ is mainly composed of the $d^0$ orbitals of the $B$-site cations, with small contribution from Bi 6$p$. The metal $d$-peaks have a large band width, suggesting them to be spatially delocalized. This has been reported in the previous study and are likely to contribute to the faster electron conduction.$^{57}$

**Lattice polarization**

The polarization quanta along the $a$ direction was calculated to be 17.79–18.26 $\mu$C/cm$^2$ (Table 1), which was smaller than the spontaneous polarization, making it necessary to trace the branch of the polarization accompanied by the structural distortion. The change in polarization accompanied by the lattice distortion from the reference non-polar structure to the polar $P2_1ab$ phase of Bi$_2$WO$_6$ is shown in Figure 3. The resulting spontaneous polarization was 61.55 $\mu$C/cm$^2$. Similarly, the spontaneous polarization of quaternary compounds were
calculated and are summarized in Table 1.

All of the quaternary compounds had smaller polarization compared to Bi$_2$WO$_6$. As mentioned above, substitution of O by F in the perovskite-like (BO$_4$)$_2^-$ layers results in a structural modification that includes a shift of the B-site cations closer to the center of their octahedra. Since the perovskite-like (BO$_4$)$_2^-$ layer is largely responsible for the polarization, this effect is responsible for the suppression. Three additional F configurations were calculated for each compounds, however the values of the spontaneous polarization were consistently smaller than that of Bi$_2$WO$_6$.

**Surfaces and band energies**

Although analysis of the electronic structure through the bulk density of states can give us insight into the material properties, knowledge of the surface structures and the band alignment is necessary to consider specific chemical reactions and device applications. Therefore, we searched for stable surface structures and analysed of the absolute band energies.

Firstly, the chemical potentials meeting the stability condition of Bi$_2$WO$_6$ were obtained. Formation of Bi$_2$WO$_6$ were limited by formation of WO$_3$ and Bi$_2$O$_3$. The possible range of $\Delta \mu_{\text{Bi}}$ were $-3.7$–$0$ eV, possible range of $\Delta \mu_{\text{W}}$ were $-9.7$ to $-1.5$ eV, and possible range of $\Delta \mu_{\text{O}}$ were $-2.4$–$0$ eV, as shown in Figure 4(a). This phase diagram is in good agreement with previous studies.$^{57,60}$

It has been reported that Bi$_2$WO$_6$ exhibits heterogeneous growth with $a$ and $b$ axis showing higher growth rate, resulting in a preference for the (001) surface.$^{52,53}$ Therefore, five different (001) surfaces of Bi$_2$WO$_6$ were considered (Figure S1). The most stable surface for given chemical potentials were calculated and are presented in Figure 4(a). Within the stable region of Bi$_2$WO$_6$, Bi–O termination were dominant followed by Bi and W termination. The stability of Bi–O termination was also suggested in a previous computational study.$^{60}$ Furthermore, monolayer Bi$_2$WO$_6$ was recently synthesized and suggested to exhibit Bi–O termination.$^{23}$
Employing the favored Bi–O terminations, the absolute electron energies were calculated and are shown in Figure 4(b). The band alignment of Bi$_2$WO$_6$ is in agreement with earlier suggestions.$^{61,62}$ The VBM of the quaternary compounds had similar levels ($-6.98$–$-6.93$ eV). The higher VBM of quaternary compounds compared to Bi$_2$WO$_6$ suggest effect of F to strengthen the hybridization of Bi $s$ and O $p$ compared to Bi$_2$WO$_6$. In contrast, the CBM level differed largely by each compounds. Together with the result of the band structures (Figure 2), the absolute position of CBM is largely dependent on the B-site cation, which suggests tunability of CBM level with substitution of B-site cations.

Conclusion

In summary, first-principles calculations were performed to characterize Bi$_2$WO$_6$, Bi$_2$TaO$_5$F, Bi$_2$NbO$_5$F, Bi$_2$TiO$_4$F$_2$ and Bi$_2$SnO$_4$F$_2$. Out of four quaternary oxides, Bi$_2$SnO$_4$F$_2$ were found to be unstable, while Bi$_2$TaO$_5$F, Bi$_2$NbO$_5$F and Bi$_2$TiO$_4$F$_2$ were stable against the decomposition reactions. Substitution of O by F ions in quaternary oxides resulted in less polar octahedra structure resulting the spontaneous polarization to be suppressed. The quaternary compounds exhibit higher valence band maximum and the conduction band minimina showed a large variation. This result suggests that the valence band can be raised by adding F and that the conduction band can be tuned by replacing the B-site cation. We demonstrated that substitution of cations and anions are effective to tune the atomic and the electronic structures of Bi$_2$WO$_6$. The approach employed in this work are likely to contribute to understanding other Bi-based mixed anion compounds.

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Supporting Information Available

Details of surface structures are presented in Supporting Information.

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Figure 1: Crystal structure of $\text{Bi}_2\text{WO}_6$, $\text{Bi}_2\text{TaO}_5\text{F}$, $\text{Bi}_2\text{NbO}_5\text{F}$, $\text{Bi}_2\text{TiO}_4\text{F}_2$ and $\text{Bi}_2\text{SnO}_4\text{F}_2$. Oxygen sites were distinguished as $\text{O}_{\text{Bi-1}}$, $\text{O}_{\text{Bi-2}}$, $\text{O}_\text{W}$, $\text{O}_\text{Ta}$, $\text{O}_\text{Nb}$, $\text{O}_\text{Ti}$ and $\text{O}_\text{Sn}$. 
Figure 2: Density of states projected for (a) Bi$_2$WO$_6$, (b) Bi$_2$TaO$_5$F, (c) Bi$_2$NbO$_5$F and (d) Bi$_2$TiO$_4$F$_2$. O$_{Bi}$, O$_{W}$, O$_{Ta}$, O$_{Nb}$, O$_{Ti}$ are oxygen atoms near Bi, W, Ta, Nb and Ti, respectively.
Figure 3: Change in polarization accompanied with the distortion of WO$_6$ octahedra from the fictitious non-polar structure to the $P2_1ab$ symmetry.

Graphical TOC Entry

TOC placeholder
Figure 4: (a): Surface phase diagram drawn as a function of the chemical potentials of Bi and W. The stable area for Bi$_2$WO$_6$ is shown as an area surrounded by the black line labeled Bi$_2$WO$_6$, WO$_3$ and Bi$_2$O$_3$. (b): Band alignment for four compounds.