Electronic properties and crystal structures of double-perovskites, Ba$_2$Bi$_{III}$Bi$_{V}$O$_6$, Ba$_2$PrBiO$_6$, and Ba$_2$PrSbO$_6$: First-principles study

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Abstract

In recent experiments, a significant band gap widening was observed when Sb was substituted for Bi in the double-perovskite Ba$_2$PrBiO$_6$. In this work, we study a series of double-perovskites, Ba$_2$Bi$_{III}$Bi$_{V}$O$_6$, Ba$_2$PrBiO$_6$, and Ba$_2$PrSbO$_6$ using the first-principles density functional theory with the Heyd-Scuseria-Ernzerhof hybrid functional to investigate the substitution effect on the structural and electronic properties. We find that the two topmost valence bands are disappeared on the substitution of Pr$_{III}$ for Bi$_{III}$, and the two bottommost conduction bands are disappeared on the substitution of Sb$_{V}$ for Bi$_{V}$, causing the significant band gap widening. Further, our calculation suggests that the Ba$_2$PrPrBiO$_6$ is a possible candidate as a source of the Pr$_{IV}$ signal observed in the experiment. We find that the B-site disordering atomic configuration, Ba$_2$B$_{IV}$V$_{III}$O$_6$, are restored to those of the original structures. On the other hand, our results also suggest the importance of the partial B-site disorder to explain the experimentally observed band gaps.

1. Introduction

TiO$_2$ is well known as an efficient photo catalytic material and has a wide range of application area from air-purifier to antimicrobial coating [1–6]. However, TiO$_2$ uses only the ultraviolet ray which is less than 3% of the whole sunlight pouring on the Earth surface. Therefore extensive studies have been devoted to develop photocatalytic materials sensitive to visible light that makes up 50% of the sunlight. A large number of double-perovskite oxides, A$_2$B$_{III}$B$_{V}$O$_6$, have been studied due to their intriguing physical and chemical properties originating in their mixed valence nature [7]. Above all, Ba$_2$PrBiO$_6$ was found to show an efficient photo catalytic activity to dissolve water molecules into oxygen and hydrogen gases under the visible light [8, 9]. Recent experiment on the Ba$_2$PrSbO$_6$ suggests the presence of the typical B-site ordering and the band gap modification [10, 11]. However, detailed theoretical analysis on the electronic structures and the crystal geometries of the double-perovskites has not been performed. In this work, we study the structural and electronic properties of Ba$_2$Bi$_{III}$Bi$_{V}$O$_6$, Ba$_2$PrBiO$_6$, and Ba$_2$PrSbO$_6$ double-perovskites using the first-principles density functional theory. The Heyd-Scuseria-Ernzerhof hybrid functional was applied to the calculations to handle the strong electron-correlation. We find that the Bi$_{III}$ 6s states at the top of valence band of Ba$_2$Bi$_{III}$Bi$_{V}$O$_6$ vanish on the Pr substitution for Bi at B$_{III}$-site. When Sb is substituted for Bi at B$_{V}$-site, the Bi$_{V}$ 6s states at the bottom of the conduction band vanish causing additional widening of the band gap. Further, our calculation suggests that the Ba$_2$PrPrBiO$_6$ is a possible candidate as a source of the Pr$_{IV}$ signal observed in the experiment. We find that the B-site disordering atomic configurations, Ba$_2$B$_{IV}$V$_{III}$O$_6$, are easily restored to those of the original structures. This demonstrates the stability of the B-site ordering in the double-perovskite framework. On the other hand, our results also suggest the importance of the partial B-site disorder in the double-perovskites to explain the experimentally observed band gaps.
2. Calculation method

We use the density functional theory (DFT) as implemented in the Vienna ab-initio Simulation Package (VASP) [12] and the projector augmented wave (PAW) potentials [13] to study the structural and electronic properties of the double perovskite. It has been known that standard exchange-correlation functionals, such as the local density approximation (LDA) and the generalized gradient approximation (GGA), predict the electronic properties of double perovskites as metal or semi-metal with a very narrow band gap [14]. Theoretical study considering the electron correlations through the GGA + U method showed an improvement on the optimized structural and electronic properties of Ba₂BiIIIIBiVO₆ [15]. However, since the method utilizes specially tuned parameter U, application of the method to the other double-perovskites is not straightforward. On the other hand, recently developed Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) [16, 17] is known to have an ability to account for the strong correlation effects and has been successfully applied to analyze the structural and electronic properties of the double-perovskites [18]. Therefore we use the HSE06 functional throughout our study. We use an energy cutoff of 500eV for plane wave basis set together with a $6 \times 6 \times 6$ k-point grid. The rather high energy cutoff and dense $k$-point grid are necessary to predict correctly the crystal structures in the HSE06 computations. Equilibrium crystal structures were achieved so that the maximum force component was smaller than 1 meV/Å³, and the maximum stress component smaller than 1 meV/Å³. Optimized crystal structures were visualized using the VESTA [19].

3. Results and discussion

First of all, we evaluate the structural and electronic properties of Ba₂BiIIIIBiVO₆ as it gives the basis in analyzing the double perovskite crystals [20, 21]. Unit cell contains four BaBiO₃ chemical units where the BiIII octahedra and the BiV octahedra are arranged alternately forming the $B$-site ordering. It has the monoclinic $I2/m$ symmetry at room temperature [22], and which is equivalent to the conventional setting of $C2/m$ No.12 [23, 24]. The $I2/m$ cell is outlined on the $C2/m$ supercell in the figure 1.

Where the distortions of octahedra caused by the mixed valencies are characterized by breathing distortion $\delta$ and tilting angle $\phi$ as depicted in figure 2.

Structural optimization has been done for the room temperature phase of $C2/m$ (table 1). Lattice constants optimized within PBE are significantly overestimated thereby causing the overestimation of $v_0$. On the other hand, HSE06 correctly predicts not only the lattice constants but also the internal distortion parameters, $\delta$ and $\phi$. The difference is even clear when we calculate the electronic property of the system: Ba₂BiIIIIBiVO₆ is semimetallic in the PBE functional while it opens band gap significantly when we use the HSE06 functional consisting...
Next, we calculate the electronic band structure. In a monoclinic system, the shape of the Brillouin zone depends non-trivially on the lattice vectors [27]. In fact, there are five possible shapes of Brillouin zones for the monoclinic crystal structure depending on the choice of lattice vectors [28, 29]. We choose the C2/m which corresponds to the MCLC1 lattice as defined in [29]. To generate the set of k-points along the edges of the Brillouin zone, we use the code pymatgen [30].

High resolution band structures and electronic density of states curves were obtained thorough the WANNIER90 package by constructing maximally localized Wannier functions (MLWFs) [31–34] using the VASP2WANNIER90 interface [35] (figure 3). The band gap is indirect and $E_{\text{I}}(\Gamma \rightarrow Z) = 0.84$ eV while the direct band gap is $E_{\text{d}} = 2.02$ eV. Electron distributions of the valence band maximum (VBM) and of the conduction band minimum (CBM) evaluated at the $\Gamma$ point are shown in the figure 4. We can see the 6s electrons of BiIII and the O 2p electrons at the VBM state (Figure 4(a)) reflecting their valence states while the 6s electrons of BiV are visible at the CBM state (figure 4(b)).

We substituted Pr for the BiIII to form Ba$_2$PrBiO$_6$. The optimized structural parameters show an excellent agreement with the experiments (table 2). Electronic band structure is given in the figure 5. The band gap is indirect $E_{\text{I}}(Z \rightarrow \Gamma) = 3.58$ eV and the direct band gap is $E_{\text{d}} = 3.70$ eV. It is visible that the two isolated valence bands near the fermi level are now vanished. The breathing distortion $\delta$ as well as the tilting angle $\phi$ retain the values before the substitution reflecting the preservation of their valence states (Ba$_2$Pr$_{\text{III}}$Bi$_{\text{V}}$O$_6$).

It has been reported that experimentally prepared Ba$_2$PrBiO$_6$ sample exhibits the valence mixing between PrIII and PrIV [10, 11]. In the experiment, the valence state PrIV was gradually suppressed as the amount of substitution of Sb for Bi was increased, and was completely resolved in the Ba$_2$PrIIISbVO$_6$ sample. However, the valence state PrIV must be compensated locally to keep the charge neutrality. One of the potential candidates for the compensation is the locally generated B-site disorder. We construct the structure by exchanging the atomic positions of Pr and Bi (Ba$_2$Pr$_{\text{III}}$Bi$_{\text{V}}$O$_6$ → Ba$_2$Bi$_{\text{III}}$Pr$_{\text{IV}}$O$_6$) while fixing the framework made by Ba and O atoms.

After the optimization, the structure recovered to that of the Ba$_2$Pr$_{\text{III}}$Bi$_{\text{V}}$O$_6$ by adjusting the distances from Pr and Bi to the nearest oxygen atoms and the valence state PrIV was not be realized. Next, we investigated the

### Table 1. Structural parameters of Ba$_2$Bi$_{\text{III}}$Bi$_{\text{V}}$O$_6$. Lattice parameters ($a$, $b$, and $c$) and the angle $\beta$ in the monoclinic C2/m cell extrapolated from those of the C2/m cell are presented. Cell volume per chemical formula unit is $v_0$. $\delta$ and $\phi$ are the breathing distortion and the tilting angle, respectively.

|          | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (deg) | $v_0$ (Å$^3$) | $\delta$ (Å) | $\phi$ (deg) |
|----------|---------|---------|---------|---------------|---------------|--------------|-------------|
| HSE06 (This work) | 6.201   | 6.150   | 8.681   | 90.35         | 82.77         | 0.10         | 11.1        |
| PBE (This work)    | 6.276   | 6.228   | 8.793   | 90.27         | 85.93         | 0.14         | 12.4        |
| HSE06*          | ...     | ...     | ...     | 90.24         | 82.10         | 0.09         | 11.9        |
| PBE*           | ...     | ...     | ...     | 90.16         | 85.76         | 0.07         | 12.1        |
| Exp1*           | 6.1814  | 6.1360  | 8.6697  | 90.173        | 82.21         | 0.085        | 11.2        |
| Exp2*           | 6.1908  | 6.1450  | 8.6785  | 90.164        | 82.54         | 0.166        | 9.43        |
| Exp3*           | 6.1851  | 6.1322  | 8.6585  | 90.229        | 82.10         | 0.180        | 10.30       |

* Values were calculated in the optimized structure derived from the cubic high temperature phase (Fm$\bar{3}$m) [14].

* Experimental data at room temperature [21].

* Experimental data at 295 K [26].

* Experimental data at 200 K [22].

with the experiment. It has been argued that this shortcoming of the PBE comes from lesser ability in describing the exchange correlation effect of strongly-correlated electron system [18, 25].

Figure 2. Distorted octahedra of Ba$_2$Bi$_{\text{III}}$Bi$_{\text{V}}$O$_6$. Where $\phi$ is defined as the average tilting angle of the neighboring Bi$_{\text{III}}$O$_6$ and Bi$_{\text{V}}$O$_6$ from the dotted line which is equal to the c-axis of the I$\bar{2}$/m cell. $\delta = \frac{1}{2} | \langle \text{Bi}_{\text{III}}\text{O}_6 - \text{Bi}_{\text{V}}\text{O}_6 \rangle |$ is defined as the breathing distortion, with Bi$_{\text{III}}$O$_6$ and Bi$_{\text{V}}$O$_6$ average Bi$_{\text{III}}$-O and Bi$_{\text{V}}$-O distances, respectively [14].

Figure 3. Electron density isosurface of Ba$_2$Pr$_{\text{III}}$Bi$_{\text{V}}$O$_6$. The Brillouin zone is shaded in black while the Fermi level is shown in the dotted line. Figure 4. We can see the 6s electrons of Bi$_{\text{III}}$ and the O 2p electrons at the VBM state (Figure 4(a)) reflecting their valence states while the 6s electrons of Bi$_{\text{V}}$ are visible at the CBM state (figure 4(b)).
Figure 3. Band structure and density of states curve of Ba$_2$Bi$_{III}$Bi$^V$O$_6$. Fermi level is at 0 eV.

Figure 4. The Bi$_{III}$ 6s orbitals are visible at the middle points of the upper and lower sides, and at the four corners of the cell in the VBM charge density distribution (a) while those of Bi$^V$ appear at the middle points of left and right sides, and at the center of the cell in the CBM charge density distribution (b). The wire-frame representation for the C$2$/m atomic arrangements (figure 1) is used to improve the visibility. Where some of the orbitals are showing their sections at the boundaries of the unit cell.

Table 2. Structural parameters of Ba$_2$PrBiO$_6$. The same notations for columns of the table 1 are used.

|       | a (Å) | b (Å) | c (Å) | $\beta$ (deg) | $\nu_0$ (Å$^3$) | $\delta$ (Å) | $\phi$ (deg) |
|-------|-------|-------|-------|---------------|----------------|--------------|--------------|
| This work | 6.211 | 6.169 | 8.707 | 90.41         | 83.41          | 0.12         | 11.1         |
| Exp1$^a$ | 6.204 | 6.169 | 8.701 | 90.27         | 83.20          |              |              |
| Exp2$^b$ | 6.201 | 6.158 | 8.697 | 90.08         | 83.03          |              |              |

$^a$ Reference [11].

$^b$ Reference [23].
substitution defect of PrBi to see if the B-site ordering is preserved by forming the Ba$_2$PrIVPrBiVO$_6$. After the structural optimization, all the distances between Pr and neighboring oxygen atoms became to be 2.33 Å ($\delta = 0$) as the result of the single valency formation of PrIV (Ba$_2$PrIVPrBiVO$_6$). It has a similar structural feature of the cubic BaPrIVO$_3$ (high temperature phase, space group $Pm\bar{3}m$) [36] except the rather elongated Pr-O bond length and the residual tilting angles. We found that the total energy of Ba$_2$Pr$_2$BiVO$_6$ per BaPrO$_3$ chemical unit is lower than that of the cubic BaPrO$_3$. Our calculation suggests that the Ba$_2$Pr$_2$BiVO$_6$ is a possible candidate as a source of the PrIV signal observed in the experiment, where the residual Bi may contribute to form Ba$_2$Bi$^{III}$BiVO$_6$.

We now focus on the substitution of the smaller ion SbV for BiV. The stable crystal structure is $R\bar{3}$. Again, the optimized crystal structure shows excellent agreement with the experimental one (table 3).

The distances from Pr and Sb to the nearest neighbor oxygen atoms are almost identical to those of the Ba$_2$PrBiO$_6$, reflecting the formation of the valence state of Ba$_2$Pr$^{III}$Bi$^{V}$O$_6$. We also tried to create the B-site disordered structure by interchanging the atomic positions of Pr and Sb in Ba$_2$PrSbO$_6$. Structural optimizations were performed only for the atomic positions while fixing the cell shape and the cell volume. The system again restores its crystal symmetry demonstrating the stability of the B-site ordering of the Ba$_2$Pr$^{III}$Sb$^{V}$O$_6$ framework.

The electronic band structure is shown in the figure 6. The BiV bands located at the bottom of the conduction bands of Ba$_2$Pr$^{III}$Bi$^{V}$O$_6$ are vanished and the band gap is widened. The calculated indirect band gap is $E_i(Z \rightarrow L) = 5.90$ eV and the direct band gap is $E_d = 5.97$ eV. Experimentally estimated band gap $E_{ex}$ also show the similar widening tendency on the substitution of Sb for BiV ($E_{ex}$(Ba$_2$PrBiO$_6$) = 0.977 eV $\rightarrow$ $E_{ex}$ (Ba$_2$PrSbO$_6$) = 2.395 eV [11]). However, the experimental values are about half of the theoretical values obtained in this work.

The hybrid functional HSE06 incorporates the short-range Hartree–Fock type exchange at the fraction of $\alpha$ (0 $\leq$ $\alpha$ < 1). It has been reported that the parameter $\alpha$ is somewhat material-specific and the best value often deviates from the standard value of $\alpha = 0.25$ [18, 27, 35]. Therefore we calculated the band gaps for $\alpha = 0.25$, 0.1, and 0.05 to see if it is the case for the double-perovskites (table 4).

The band gaps of Ba$_2$Bi$^{III}$Bi$^{V}$O$_6$ calculated with the small $\alpha$ significantly deviate from the experimental ones while those of the Ba$_2$Pr$^{III}$Bi$^{V}$O$_6$ and Ba$_2$Pr$^{IV}$Sb$^{V}$O$_6$ show decreasing tendency with decreasing the $\alpha$ but are still larger than the experimental values. We can conclude that the adoption of the smaller $\alpha$ does not improve the

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**Table 3.** Structural parameters of Ba$_2$PrSbO$_6$. The same notations for columns of the table 1 are used.

|      | $a$ (Å) | $\alpha$ (deg) | $v_0$ (Å$^3$) | $\delta$ (Å) | $\phi$ (deg) |
|------|---------|----------------|---------------|--------------|--------------|
| This work | 6.075   | 60.00          | 78.65         | 0.16         | 6.3          |
| Expt.$^a$ | 6.047   | 60.16          | 78.64         |              |              |

$^a$ Experimental value [11].

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**Figure 5.** Band structure and density of states curve of Ba$_2$Pr$^{III}$Bi$^{V}$O$_6$. Two isolated valence bands near the Fermi level of Ba$_2$Bi$^{III}$Bi$^{V}$O$_6$ were vanished due to the B$^{III}$-site substitution.
On the other hand, we focus on the partial disorder of the B-sites as it has been experimentally found in the Ba$_2$Pr$_{IIIB}$BiVO$_6$ sample $^{23}$. Although our calculation indicates that the B-site disordered double-perovskites are energetically unfavorable, it does not exclude the possibility of the presence of partial disordered B-sites in the ordered double-perovskite matrices. It is well known that the electronic properties of semiconductors are easily modified significantly by incorporation of small amounts of impurities or other kind of defects $^{39}$. We evaluated the band gaps of the B-site disordered double-perovskites using the standard value for the $\alpha$ (table 4). Structural relaxations were not performed. We found fluctuating behavior both in the lowest conduction band and the highest valence band thereby significantly narrowing their band gaps. The indirect band gap of the B-site disordered Ba$_2$Pr$_{IIIB}$BiVO$_6$ is $E_d = 0.78$ eV which is comparable to the experimental value of 0.977 eV. Similarly, the direct band gap of the B-site disordered Ba$_2$Pr$_{IIISb}$BiVO$_6$ is $E_d = 1.89$ eV which is also comparable to the experimental value of 2.395 eV. Although the B-site disordering of the Ba$_2$Pr$_{IIISb}$BiVO$_6$ has not been observed in the experiments yet, our results indicate that the B-site disordering atomic configurations in the double-perovskites may control their band gaps.

Table 4. HSE06 band gaps (eV) calculated for the $\alpha = 0.25$, 0.1, and 0.005. Experimental band gaps are also shown (Expt.). Band gaps of B-site disordered double-perovskites, Ba$_2$ (Pr$_{III}$ $\rightarrow$ Bi$^V$)O$_6$ and Ba$_2$ (Pr$_{III}$ $\rightarrow$ Sb$^V$)O$_6$ without structural relaxations, are also shown.

|    | HSE06 | Expt. |
|----|-------|-------|
|    | $\alpha = 0.25^a$ | $\alpha = 0.1$ | $\alpha = 0.05$ | $E_d$ | $E_i$ | $E_d$ | $E_i$ | $E_d$ | $E_i$ | $E_d$ | $E_i$ |
| Ba$_2$Bi$_{III}$Bi$^V$O$_6$ | 2.02 | 0.84 | 1.55 | 0.50 | 1.40 | 0.39 | 2.0$^b$ | 0.2$^c$ | 2.07$^d$ | 0.84$^d$ |
| Ba$_2$Pr$_{III}$Bi$^V$O$_6$ | 3.70 | 3.58 | 2.82 | 2.77 | 2.54 | 2.50 | 0.977$^e$ |
| Ba$_2$ (Pr$_{III}$ $\rightarrow$ Bi$^V$)O$_6$ | 1.14 | 0.78 | | | | | | |
| Ba$_2$Pr$_{III}$Sb$^V$O$_6$ | 5.97 | 5.90 | 4.94 | 4.90 | 4.61 | 4.55 | 2.395$^f$ |
| Ba$_2$ (Pr$_{III}$ $\rightarrow$ Sb$^V$)O$_6$ | 1.89 | 1.09 | | | | | | |

$^a$ Standard value used in the HSE06 calculation.
$^b$ Reference [37].
$^c$ Reference [38].
$^d$ Reference [14].
$^e$ Reference [11].

$^f$ References [11].
4. Conclusion

Density functional calculations were performed to investigate the structural and electronic properties of the double-perovskites, Ba₂Bi²⁺III⁻Bi⁶⁺O⁶, Ba₂PrBiO₆, and Ba₂PrSbO₆. The B-site ordering in the Ba₂Bi²⁺III⁻Bi⁶⁺O⁶ creates typical electronic band structure, where the top of the valence bands are composed of Bi³⁺ ⁶s orbitals while the bottom of the conduction bands are composed of Bi⁶⁺ ⁶s orbitals. By substituting the Pr for Bi³⁺, two valence band originated in the Bi³⁺ ⁶s orbitals are vanished thereby widening the band gaps. Substitution of Sb for Bi⁶⁺ induces additional band gap widening. Further, our calculation suggests that the Ba₂PrPr₈O₆ is a possible candidate as a source of the Pr⁴⁺ signal observed in the experiment. The B-site disordering atomic configurations are restored to those of the original crystal structures. It demonstrates the stability of the B-site ordering in the double-perovskite framework. However, it does not exclude the presence of the partial B-site disordering as it has been experimentally observed in the Ba₂Pr₃III⁻Bi⁶⁺O₆ sample. Calculated band gaps for the B-site disordered Ba₂Pr²⁺III⁻Bi⁶⁺O⁶ and Ba₂Pr²⁺III⁻Sb⁶⁺O₆ show comparable results with the experiments. Although the B-site disordering of the Ba₂Pr²⁺III⁻Sb⁶⁺O₆ has not been observed in the experiments yet, our results indicate that the B-site disordered atomic configurations in the double-perovskites may play an important role to adjust their band gaps.

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