

# First-principles band calculation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with orthorhombic structure

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## Abstract

First,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  unit cell is optimized by relaxing all the lattice constants and atomic positions using the Cambridge Serial Total Energy Package (CASTEP) code within the framework of generalized gradient approximation (GGA). Then, the electronic structure calculation of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is performed by using the scalar-relativistic full potential linearized augmented plane wave + local orbital (FLAPW+*lo*) method. As a result, the valence band maximum (VBM) is located on the  $\text{Y}\Gamma$ -line and the conduction band minimum (CBM) at the  $\Gamma$ -point, indicating that  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is an indirect energy gap material. The minimum gap of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is estimated to be 2.50 eV. Density of states analysis shows that the valence band of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is dominated by competing interactions between Ti and O and Bi-O, while the conduction band is dominated by interactions between Ti and O.

*Key words:*  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , First-principles, Energy band calculation, Density of states

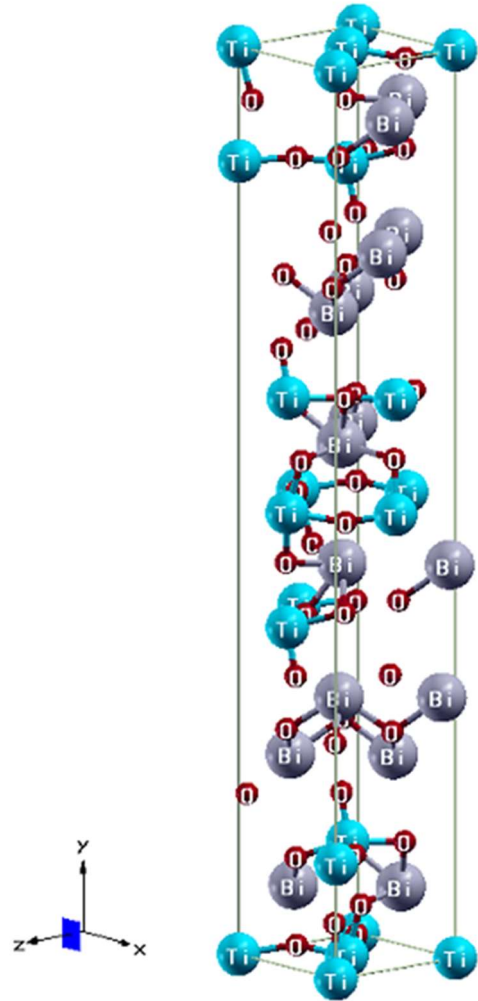
## 1. Introduction

There are five kinds of bismuth titanate compounds with the stoichiometric chemical composition in the  $\text{Bi}_2\text{O}_3$ – $\text{TiO}_2$  system. They are  $\text{Bi}_2\text{Ti}_2\text{O}_7$ ,  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{Bi}_8\text{TiO}_{14}$ , and  $\text{Bi}_{12}\text{TiO}_{20}$ . These crystal phases were identified by Bruton and Masuda *et al* [1-3]. Among them,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is a thermodynamically stable and has been attracting attention for a long time due to its ferroelectric properties [3]. In recent research,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is attracting attention as a photocatalyst, since it can efficiently separate electrons and holes photo-generated [4, 5]. To understand the mechanisms of the ferroelectric behavior and photocatalysis, it is essential to obtain detailed information on the electronic structure of the solid.

In the present work, we carried out a first-principle band calculation of pure  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  with orthorhombic structure to determine the band-gap energy, the type of optical transition, and the characteristics of the valence band and conduction band by the generalized gradient approximation (GGA) calculation [6, 7].

## 2. Computational procedure

Figure 1 shows the crystal structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ .  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  crystallizes into an orthorhombic structure with space group  $Aba2$  and contains four formula units for a total of 76 atoms [8, 9]. There are two independent Bi atoms (Bi1 and Bi2), two independent Ti atoms (Ti1 and Ti2), and six independent O atoms (O1 to O6). Bi atoms occupy at the Wyckoff  $8b$  position, Ti atoms occupy at the Wyckoff  $4a$  and



**Fig. 1** Crystal structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ .

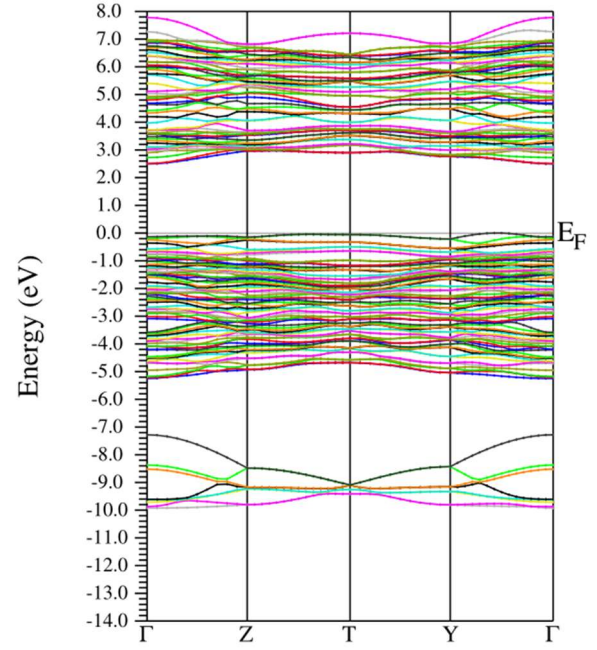
8b positions, and O atoms occupy at the Wyckoff 8b position. Also, the structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  can be understood as consisting of perovskite-type unit with  $\text{TiO}_6$  octahedra and Bi atoms (Bi1) occupying A-site and  $\text{Bi}_2\text{O}_2$  layers (Bi2) [10].

The  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  unit cell was optimized by relaxing all the lattice constants and atomic positions using the Cambridge Serial Total Energy Package (CASTEP) code [11]. The exchange and correlation interactions were treated within the framework of the GGA method proposed by Perdew *et al* [6, 7]. The cutoff energy of plane-wave expansions was chosen 380 eV. Valence electrons were treated with Vanderbilt-type nonlocal ultra-soft pseudo-potentials, which describe effective potentials of ions and tightly bound core electrons [12]. The reciprocal-space integration was carried out with 2 irreducible  $k$ -points, which correspond to  $2 \times 2 \times 1$   $k$ -points grid [13].

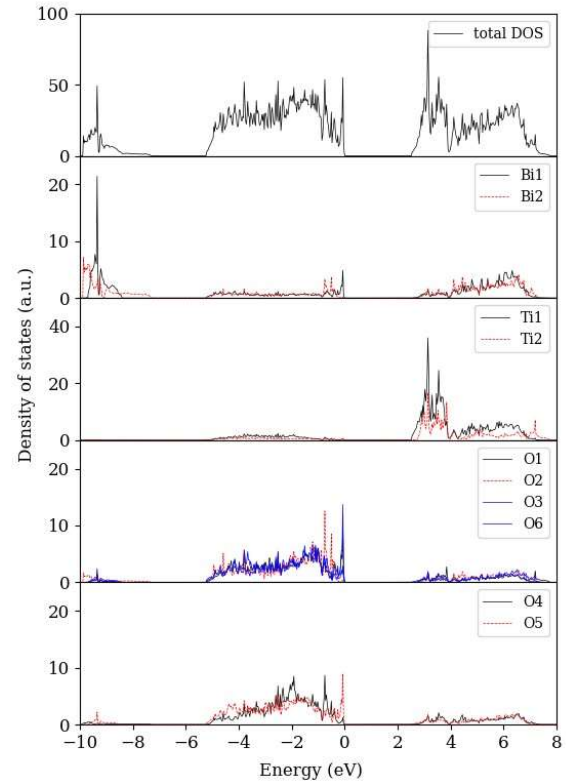
The electronic structure calculation of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  was performed by using the scalar-relativistic full potential linearized augmented plane wave (FLAPW+*lo*) method [14]. The wave functions were expanded by APW basis functions composed of plane waves in the interstitial region and linear combinations of radial function multiplied by spherical harmonics inside the muffin-tin (MT) region. The MT sphere radii ( $R_{MT}$ ) of the Bi, Ti, and O atoms were 2.20, 1.69, and 1.53 a.u., respectively. The plane wave cutoff was  $R_{MT} \cdot K_{max} = 7.0$ , which gave 5630 plane waves and 318 local orbitals for  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ .

### 3. Results and Discussion

**Figure 2** shows the calculated energy band structure along the symmetry lines of the first BZ of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  crystal obtained using the GGA approach. The origin of the energy was taken at the valence band maximum (VBM).  $\Gamma$ , Z, T, and Y are symmetry points in the first BZ. Those coordinates are respectively (0, 0, 0), (0, 0, 0.5), (0.5, 0.5, 0.5), and (0.5, 0.5, 0) in units of  $g_1^*$ ,  $g_2^*$ , and  $g_3^*$ , where  $g_1^*$ ,  $g_2^*$ , and  $g_3^*$  are the relevant reciprocal-space vectors. Although the energy difference between the direct and indirect transition is very small as shown in **Fig. 2**, the VBM is located on the Y $\Gamma$ -line and the conduction band minimum (CBM) at the  $\Gamma$ -point, indicating that  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is an indirect energy gap material. The minimum gap of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  was estimated to be 2.50 eV. This value is well consistent with the reported value 2.57 eV [15].



**Figure 2** Energy band structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  unit cell.



**Figure 3** Total and partial density of states of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  unit cell.

**Table 1** Bi–O and Ti–O bond lengths of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  unit cell. The bond lengths in this table are in Å.

No.	Bi1	Bi2	Ti1	Ti2
1	2.23994	2.13063	1.85235	1.71829
2	2.31447	2.31224	1.85235	1.93083
3	2.36006	2.36506	2.00906	1.98491
4	2.46734	2.42357	2.00906	1.98686
5	2.51286	2.53064	2.03712	2.08926
6	2.61822	2.69262	2.03712	2.33085
7	2.86709	3.11165		
8	2.89279	3.24944		
9	3.05564	3.31716		
10	3.14644	3.56599		
11		3.65877		
Average	2.64749	2.85071	1.96618	2.00683

**Figure 3** shows the total density of states (TDOS) and partial density of states (PDOS) for each constituent atom in  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  crystal. The origin of the energy in **Fig. 3** was chosen to accord with that in **Fig. 2**. As seen in the TDOS, the VB lies in the range from  $-9.9$  to  $-7.3$  eV and from  $-5.2$  to  $0$  eV, and the conduction band is distributed above  $2.5$  eV.

PDOS of Bi1 is dissimilar to that of Bi2 owing to the different coordination geometry as listed in **Table 1**; Bi1 is coordinated by ten oxygen at av.  $2.6475$  Å (O1, O3, O5, and O6), and Bi2 is located at a site eleven-coordinated by oxygen at av.  $2.8507$  Å (O2, O4, O5, and O6). On the other hand, Ti occupies a site six-coordinated by oxygen. Ti1 interacts with O1 and O3, and Ti2 with O3, O4, O5, and O6. As is clear from **Table 1**, the average distance of Ti–O bonds is much smaller than that of Bi–O bonds. The shorter bond length leads to the stronger interaction between Ti and O atoms than Bi and O atoms.

Additionally, the Bi 6s states are strongly localized near the top of the valence band, which corresponds to the classically known inactive electron pair of Bi 6s [16].

#### 4. Conclusion

In this study, we applied the FLAPW+*lo* method to a structure-optimized  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  unit lattice to investigate the solid-state electronic structure. The following are the findings obtained.

- 1) The VBM of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is located on the YΓ-line and the CBM at the Γ-point.
- 2) The minimum gap of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is estimated to be  $2.50$  eV.
- 3) In both the valence and conduction bands of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , Ti–O bonds are more dominant than Bi–O bonds.
- 4) Near the top of the valence band, Bi 6s states are identified that contribute to the inert electron pairing effect.

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