First-principles prediction of structural and electronic properties of $BiVO_3$

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Bismuth vanadate, whose chemical formula is $BiVO_4$, has been attracted attention for sustainable energy applications since this material shows promising results for solar hydrogen production when it is used as water-splitting photocatalyst and photoanode in photoelectrochemical cell [1]. In recent years, the ABO_3-type perovskites and related heterostructures have provided a variety of physical properties such as ferroelectricity, ferromagnetism, and multiferroicity [2]. From this perspective, it is wondering what properties could be generated if bismuth vanadate is materialized as $BiVO_3$. I thus attempt to predict the structural and electronic properties of $BiVO_3$ using first-principles calculations. Those properties are not yet reported by experiment since the synthesis of $BiVO_3$ is very difficult using conventional growth techniques such as solid-state reaction method.

In this work, first-principles calculations are based on density-functional theory and the screened hybrid functional of Heyd-Scuseria-Ernzerhof (HSE) [3,4], implemented with the projector augmented-wave method in the vasp code [5]. The mixing parameter in the HSE (i.e., amount of the nonlocal Fock-exchange) was set to 25%. I have performed bulk calculations for $BiVO_3$ and nominal form, $BiVO_4$ is also considered for comparison. Two $BiVO_4$ phases (monoclinic: $I2/b$ [convertible to a space group of C2/c with a body-centered cell] and tetragonal structure: $I4_1/a$) and $BiVO_3$ (cubic perovskite: $Pm3m$) are studied.

Figure 1 shows crystal structures of $BiVO_4$ and $BiVO_3$. The unitcells contain 20 atoms for $BiVO_4$ and five atoms for $BiVO_3$. The calculated lattice parameters of monoclinic $BiVO_4$ are a = 5.09 Å, b = 5.15 Å, and c = 11.66 Å, and those of tetragonal form are a = 7.32 Å and c = 6.43 Å. These HSE results are in good agreement with the experimental values. For the cubic $BiVO_3$, the lattice constant is computed to be 3.85 Å. Moving to the electronic structure of $BiVO_3$, which is a main concern, our calculations predict the metallic-like band structure [Figure 2], resulting from two extra electrons that do not participate in chemical bonds. When the electrons are intentionally removed in the calculations, $BiVO_3$ exhibits an insulating behavior with the band gap of 2.9 eV at X-point. It is noteworthy that the ferromagnetic phase of $BiVO_3$ is more stable than the simple metallic state of it by 0.8 eV per formula unit. Therefore, various magnetic phases will be examined in a following study.

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References

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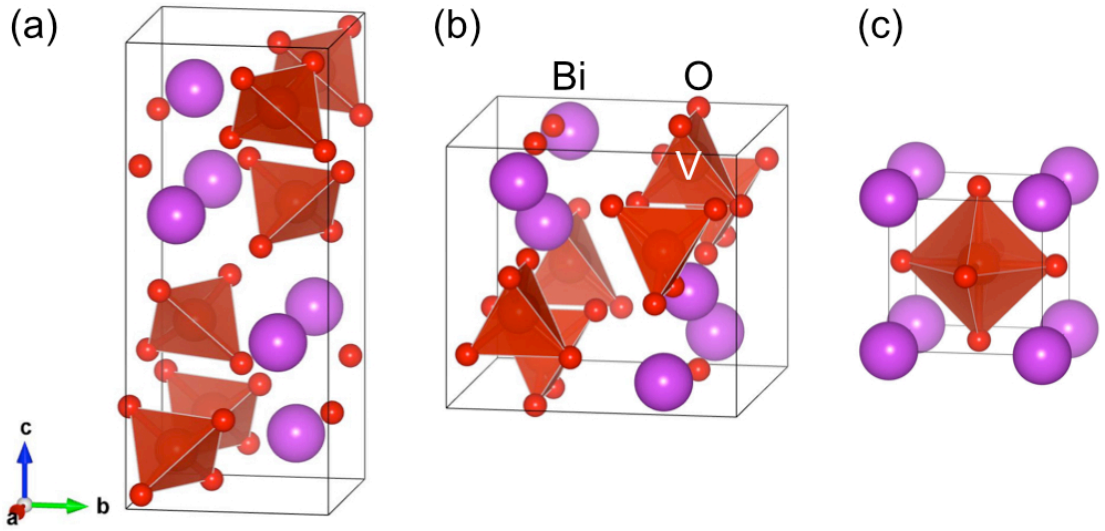

FIG. 1. Crystal structures of (a) monoclinic $BiVO_4$, (b) tetragonal $BiVO_4$, and (c) cubic perovskite $BiVO_3$. Magenta and red balls denote bismuth and oxygen atoms, respectively. Ball in polyhedrals is vanadium.

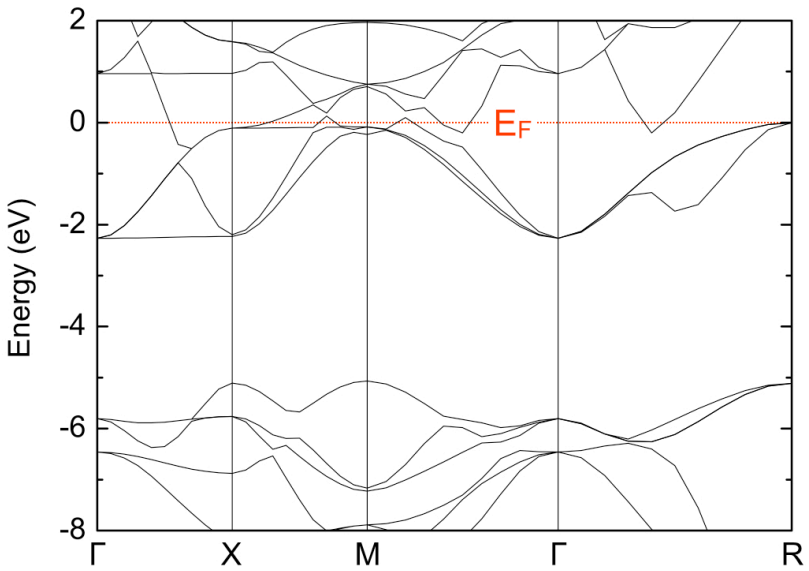

FIG. 2. Predicted band structure of cubic $BiVO_3$ using the HSE functional. The Fermi level (E_F) is set as zero.