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Computational study of band gap and structural effect of doped $BiVO_4$

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Abstract. Density functional theory calculation using Quantum Espresso package was conducted to study band gap and structural effect of $BiVO_4$ by doping elements like Zr, Mo and S, to substitute Bi, V and O. Band gap of $BiVO_4$ has been reduced from 2.25 to 1.54 eV by ~8% S^{2-} substitution with O^{2-}. Distance between atoms V-O increased by changing to V-S, which effects vibration of the atoms in the structure. ~2% substitution Mo and Zr with Bi and V changed monoclinic $BiVO_4$ to mix phase of tetragonal scheelite phase. It has been shown that XRD powder pattern of optimized structure can show (121) plane peak shifts by doping Mo or Zr in $BiVO_4$ lattice.

1 Introduction

Photoelectrochemical (PEC) water-splitting one of the promising strategies of solar hydrogen production. Since first PEC worked with of TiO2 as a photoanode in 1972 [1], several alternative semiconductor materials have been investigated as potential photoanodes. BiVO4 emerges as a promising candidate due to its narrow bandgap, non-toxicity, high stability, and exceptional photocatalytic properties [2-4]. The conduction band primarily comprises V3d, while the valence band is formed by the hybrid orbitals of Bi6s and O2p, facilitating hole transport to the surface [5]. Despite its notable photocatalytic activity, unmodified BiVO4 has yet to achieve optimal efficiency due to its relatively wide bandgap and poor charge separation.

Doping represents a straightforward and effective approach to improve O_2 evolution [6-7]. Both anion and cation doping are viable options for enhancing $BiVO_4$ [8]. Experimental investigations have demonstrated that anion doping boosts the photocatalytic efficiency of $BiVO_4$ by reducing its bandgap and increasing the rate of photocarriers [9-11]. $BiVO_4$ has another two doping sides: Bi and V. Partial substitution with other metals proves more stable than anionic substitution [12-13]. Introducing Mo^{6+} and W^{6+} as n-type dopants into $BiVO_4$ to replace V^{5+} enhances its electrical conductivity [14-15]. Zr^{4+} can substitute either Bi or V atoms in the $BiVO_4$ lattice, with potentially lower formation energy for Bi substitution due

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to better electronic and ionic configuration compatibility [16]. Zr, with an ionic radius close to that of Bi^{3+}, could mimic the photocatalytic effect observed with Mo or W doping in $BiVO_4$ upon tetravalent Zr^{4+} substitution for trivalent Bi^{3+} [17].

Density functional theory (DFT) calculation is one the effective study for structural and electron density states analysis [18]. Some works in DFT study was presented to understand electronic structure of $BiVO_4$ and band gap type of the $BiVO_4$ photoanode [19].

In this works, computational study of effect of S, Mo and Zr doping into monoclinic BiVO4 structure was studied. DFT calculation was used to optimize doped $BiVO_4$ structure and to investigate its band structure.

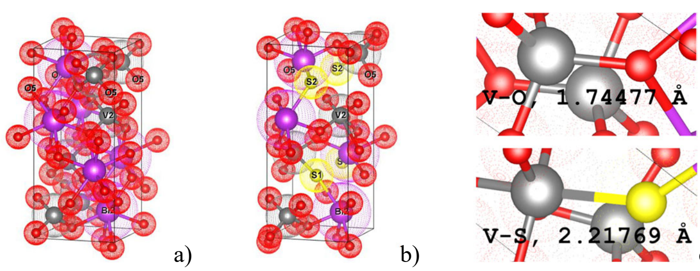
2 Methods

Density functional theory (DFT) simulations are carried out, using Quantum ESPRESSO while the results are visualized on VESTA. The experimentally observed crystallographic file of $BiVO_4$; monoclinic structure was used with lattice parameters of a = 7.330 Å, b = 11.811 Å, c = 5.149 Å, α = β =90°, and γ = 134.227°. In the optimization of the structure, a kinetic energy of 45 Ry and a charge density of 455 Ry were set for the wave function. 4×4×4 k width, Gaussian localization, ultrasoft pseudopotential, and Perdew−Burke−Ernzerhof (PBE) functions were used in the calculation process.

3 Results and discussion

3.1 S doping into $BiVO_4$

A unit cell of monoclinic $BiVO_4$ (CIF) was taken to calculate electronic structure; undoped and S (~8%) doped $BiVO_4$ was optimized using Quantum ESPRESSO pack and visualized by VESTA (Figure 1a). After S doping structure of $BiVO_4$ was kept as monoclinic, with changing gamma angle from 90.1034 to 88.9054 degree (Figure 1c), volume of the structure was increased from 314.0718 Å^3 to 341.9792 Å^3.



a) b) c)

Fig. 1. Visual structure of optimized undoped (a) and S doped (b) monoclinic BiVO4, the distance between V-O and V-S in pure and S doped $BiVO_4$.

S doping into $BiVO_4$ is interesting with substituting O in the lattice to decrease its band gap to increase number of photoexcited electrons from the valence band (VB) to conduction band (CB). Greater ionic radii of S than O, make shift VB upward and decreases band gap. In Fig. 2, Density of states (DOS) of undoped and S doped $BiVO_4$ has been shown. It can be seen that VB is mainly consisted by O and Bi states and CB is consisted by V. After S incorporation VB band showed effect of S states and also decreasing band gap due to VB shift. Fermi level was fixed to 0 position and it was shifted to CB side. This effect is explained as being more electrons on the CB side due to VB shift by S doping, and it might increase migration of electrons, results more charge separation to increase photocurrent of $BiVO_4$ photoanode [8-9].

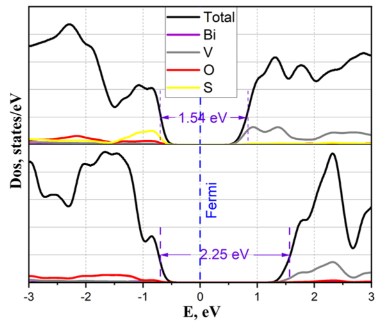


Fig. 2. DOS undoped (down) and S doped (up) monoclinic $BiVO_4$.

3.2 Mo and Zr doping into $BiVO_4$

Replacing S^{2-} with O^{2-} may affect band gap to increase photocatalytic effect of $BiVO_4$ without changing oxidation states of elements directly. However, doping Mo^{6+} or Zr^{4+} with substituting V^{5+} or Bi^{3+}, respectively, may increase charge separation of photocarrier, results increase of photocatalytic performance [17, 19]. Different ionic radii of elements my affect structural changes. Mo and Zr doping makes impurity tetragonal phase together with monoclinic phase in the experimental works [14, 17]. Structural changes or phase changes may affect photocatalytic properties of photoanodes.

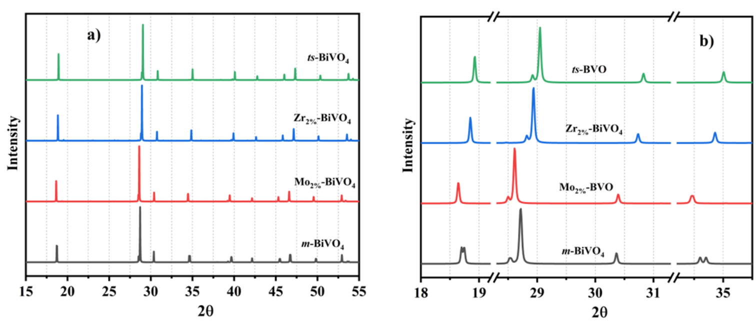


Fig. 3. X-ray powder pattern of optimized Mo and Zr doped $BiVO_4$, with comparison its monoclinic and tetragonal phase: wide range (a) and specific range (b) phase peaks.

We doped Mo and Zr into $BiVO_4$ lattice with ~2% atomic percentage to study structural XRD powder patterns of $BiVO_4$ (Fig. 3a). Optimization structures presented chance to compare doped $BiVO_4$ with undoped $BiVO_4$. Even 2% Mo and Zr doping showed structural change in $BiVO_4$, pure monoclinic phase to tetragonal scheelite (Fig. 3b). However, it has been reported that high doping concentration of Mo or Zr turns to monoclinic phase to tetragonal zircon [14, 17]. Characteristic dual peaks of monoclinic $BiVO_4$ at ~18.7 and ~34.8 degree, have been merged and showed impurity phase. Also, dominant peak at ~28.5 degree of 2 theta, shifted to lower (Mo doping) and higher (Zr doping) side due to difference of ionic radii of substituted elements.

4 Conclusion

In this work, DFT calculation using Quantum ESPRESSO pack was used to calculate electronic structure of pure and S doped BiVO4 with DOS. XRD powder pattern of optimized Mo and Zr doped $BiVO_4$ was compared pure $BiVO_4$. S doping led to decreasing band gap of $BiVO_4$ due to shift VB to CB side substituting of S^{2-} with O^{2-}. It has been shown that Fermi level was shifted to CB side, due to shift of electron density by S doping. We have obtained that even 2% atomic doping of Mo and Zr affects to the monoclinic structure. Monoclinic structure turned to mix phase of tetragonal scheelite. Also, peak shift was observed to lower and higher degree toward of Zr and Mo, due to difference of ionic radii comparing Bi and V. Band gap decreasing is useful to utilize visible light of sunlight. Structural and phase change can bus used as a heterostructure of different type of materials. Both results are valuable for researcher to study photocatalytic performance of $BiVO_4$.

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