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Band gap engineering by anion doping in the photocatalyst BiTaO₄: First principle calculations

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ABSTRACT

We have shown the effect of mono and co-doping of non-metallic anion atoms on the electronic structure in BiTaO₄ using the first-principles method. It can improve the photocatalytic efficiency for hydrogen production in the presence of visible sunlight. It is found that the band gap of BiTaO₄ has been reduced significantly up to 54% with different non-metallic doping. Electronic structure analysis shows that the doping of nitrogen is able to reduce the band gap of BiTaO₄ due to the impurity N 2p state at the upper edge of the valence band. In case of C or C-S doped BiTaO₄, double occupied (filled) states have been observed deep inside the band gap of BiTaO₄. The large reduction of band gap has been achieved, which increases the visible light absorption. These results indicate that the doping of non-metallic element in BiTaO₄ is a promising candidate for the photocatalyst due to its reasonable band gap.

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1. Introduction

Suitable semiconductor electrodes and photocatalyst for the splitting of water into hydrogen and oxygen gas using solar light is one of the promising issue for material science in the frame work of future clean and renewable energy source [1–5]. Conversion of solar-in-chemical energy in the form of hydrogen via photocatalytic decomposition of water is attractive because of the abundance of water and availability of the sunlight. A few metal oxides which contain Bi such as, BiVO₄ and Bi₂WO₆ are good candidates for the efficient photocatalytic process under visible light irradiation [6,7]. Recently, band gap engineering of semiconductor materials have become

a subject of intensive research in the context of nanoscale electronics and photocatalyst for the maximum utilization of the visible light to suppress the rapid combination of photo-generated electrons and holes.

BiTaO₄ has considerable attention for the hydrogen production material from water in the presence of the sunlight. It is mainly because of the position of the band edges with respect to water redox potentials [8–10]. However, as a wide band gap semiconductor (2.75 eV), BiTaO₄ allows absorbing only 19% of the visible light spectrum which is not enough for efficient photocatalyst material. For efficient photocatalyst material, semiconductors would need to have optimal band gap around 2.0 eV. The position of the reduction

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and oxidation levels of water should lie between the valence band maximum (VBM) and the conduction band minimum (CBM) [11]. Therefore, band gap engineering has been required for improving the performance of semiconductors as a photocatalyst by the induction of electronic states. Usually, the broad spectrum of the solar energy can be used by the cation/anion doping in the wide band gap semiconductors to generate donor/acceptor states in their band gap [12–15]. Impurity states in the band gap could work as recombination center and lower the efficiency of photocatalyst. We would like to add states on the top of the valence band. According to the experimental studies, it has been found that partially occupied impurity states in the band gap can act as recombination centers, which reduces the efficiency of photocatalyst. Controlled creation of such intermediate donor or acceptor levels at the top of valence band or bottom of conduction band are highly appreciating for solar cell applications [16]. Doping of non-metallic anion elements in semiconductors such as, TiO_2 , WO_3 , and CsTaWO_6 are very effective to shift the VBM upwards and narrowing the band gap to active visible-light-driven photocatalyst [17–20]. Holes mediated dopant–dopant coupling play more effective role in the reduction of the band gap as compared to the single dopant [21,22]. Induction of disorder in the surface layers of nanophase by hydrogenation is a new approach to enhance solar absorption [23].

In this work, we present the effect of mono and co-doping of non-metallic atoms on the electronic, energetic properties and the band gap engineering in BiTaO_4 for improving the photocatalytic efficiency. We also show that the position of the occupied and unoccupied bands can be tuned by choosing different non-metallic atoms or combination of these atoms. Unoccupied states are found just above the VBM by the doping of N or N-N, whereas in the case of the C-doping, fully occupied double states lie in the middle of the band gap, which has a large effect on the optical properties of BiTaO_4 . By the doping of non-metallic atoms in the BiTaO_4 , possibility of reduction and oxidation process has also been investigated by comparing it with pure BiTaO_4 redox alignment plot.

2. Computational Details

In our work, the first-principles calculations were performed using projected augmented wave (PAW) method [24] as implemented in the Vienna ab initio simulation package (VASP) [25–27]. The exchange–correlation interaction was treated in the level of the GGA using Perdew–Burke–Ernzerhof (GGA-PBE) [28]. The Brillion zone was integrated using Monkhorst–Pack generated sets of k-points [29]. K-points mesh $3 \times 3 \times 5$ and $3 \times 5 \times 5$ found to be sufficient to reach convergence for bulk supercell and (100) surface calculations, respectively. For the assessment of the oxygen and nitrogen molecules, a $12 \times 12 \times 12 \text{ \AA}^3$ sized box was created. We had employed a plane wave basis set with an energy cutoff of 400 eV to describe the electronic wave function. The PAW potentials with the valence states 6s and 6p for Bi, 5d and 6s for Ta, 2s and 2p for O, N, C and S had been employed. In all calculations, self-consistency was achieved with a tolerance in the total energy of at least 0.01 meV. For doping cases,

a $2 \times 2 \times 1$ supercell with 96 atoms was used, where dopant complexes substituting on the O site were placed at the center of the supercell. In the conventional method, the work function (vacuum level) could be calculated as $\phi = V(\infty) - E_F$, where $V(\infty)$ and E_F are the electrostatic potential in a vacuum region far from the neutral surface and the Fermi energy of the neutral surface system, respectively [30].

3. Results and discussion

BiTaO_4 has a triclinic structure with space group P1 at ambient conditions. The calculated lattice parameters are $a = 5.57 \text{ \AA}$, $b = 7.65 \text{ \AA}$, $c = 7.73 \text{ \AA}$, $\alpha = 102.98^\circ$, $\beta = 89.91^\circ$, $\gamma = 93.36^\circ$ within GGA/PBE, in good agreement with experimental data [9]. We have studied the electronic structure of the pure BiTaO_4 using density functional theory (DFT). The calculated band gap of the pure BiTaO_4 is 2.4 eV with GGA-PBE, which is slightly under estimated the experimental band gap [8–10] due to the well known LDA/GGA errors for semiconductors and insulators [31]. The valence band has been derived mainly from the 2p states of oxygen and Bi 6p but conduction band is dominated by the Ta 5d states. The total and partial density of states of pure BiTaO_4 has been plotted in Fig. 1. This band gap is sufficiently large to overcome the endothermic character of the water-splitting reaction (requiring 1.23 eV).

The work function has been calculated using conventional method by taking the difference between electrostatic potential and fermi energy [30]. The work function for the (100) surface of BiTaO_4 is 6.3 eV. In Fig. 2, we have aligned the redox energy levels with respect to the vacuum level. Here we consider the experimental standard water reduction and oxidation levels, which are 4.44 and 5.67 eV respectively [32,33]. A schematic illustration of the DOS of bulk BiTaO_4 is shown in Fig. 2. It shows that the energy level for hydrogen reduction (H^+/H_2) exist 0.54 eV lower than the CBM, which lead to inject electrons into the solution for hydrogen production. Oxidation level ($\text{O}_2/\text{H}_2\text{O}$) exists about 0.63 eV higher the VBM, which would permit transfer of

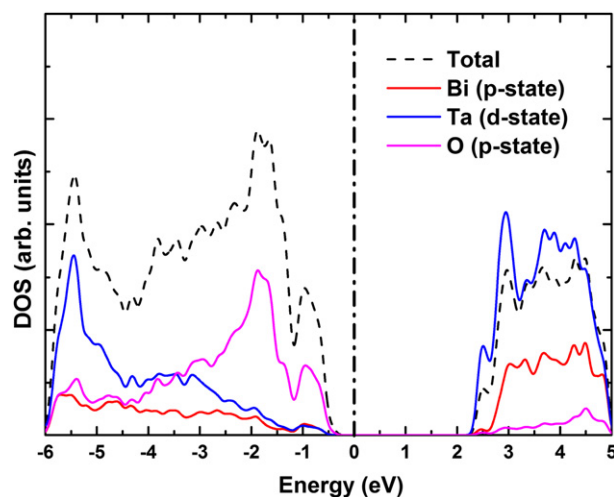


Fig. 1 – The calculated total and partial density of states for bulk BiTaO_4 .

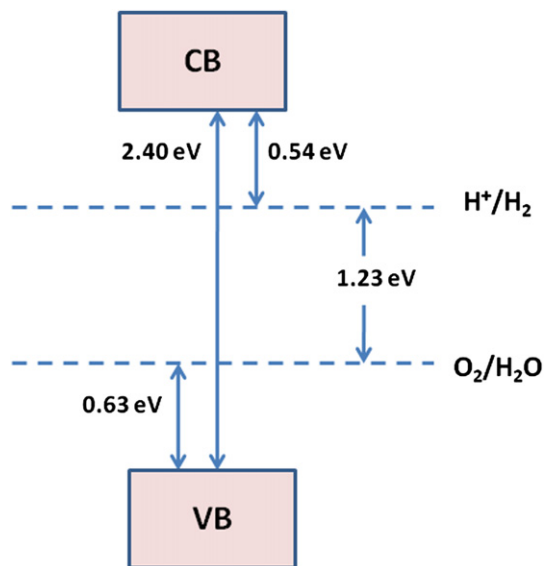


Fig. 2 – Schematic diagram of the positions of redox levels with respect to the band edges for pure BiTaO₄. The position of the redox levels of pure BiTaO₄ are indicated by the horizontal dashed lines, which are aligned with respect to vacuum level.

holes. The amount of energy equal to the band gap is required to transfer electrons from valence band to conduction band, so that holes are generated in the valence band. Both redox levels lie in the band gap, which shows that the reduction and oxidation process is energetically possible in pure BiTaO₄. These calculations show that BiTaO₄ may be used as a good candidate for the hydrogen production. But this material has two limitations, (i) Large band gap so that it absorbs very small amount of the visible light (ii) the driving force required for the redox process. To overcome these problems, we have to do the band gap engineering by the doping of non-metallic atoms to achieve efficient photocatalytic properties.

In order to elucidate the doping effect on the electronic and optical properties of BiTaO₄, single non-metallic atom (C, N and S) has been replaced with one of the oxygen atom in 96 atom supercell of BiTaO₄, which gives doping concentration ~1.56%. We have studied the electronic and energetic properties of doped BiTaO₄. The formation energy of these doping, ΔE_f is defined as the energy needs to introduce such doping in bulk BiTaO₄, which is calculated as follows [34,35]:

$$\Delta E_f = E_T(D) - E_T(H) + n\mu_O - n\mu_X, \quad (1)$$

Here $E_T(H)$ and $E_T(D)$ are the total energies of pure and doped BiTaO₄, respectively. The term n is the number of the doping atoms. μ_O and μ_X are the atomic potential of the oxygen and doped atom, respectively. The calculated formation energies required for the different doping are described in Table 1.

Substitution of N with O in BiTaO₄ lattice are found to be effective since N 2p states contribute the band gap narrowing by the mixing with O 2p states. Doping of single nitrogen generates shallow acceptor levels at the top of the valence

Table 1 – Formation energy, shifting of valence (ΔE_v) and conduction band (ΔE_c) for non-metallic doping in BiTaO₄. Positive value indicates an increase in energy with respect to the pure BiTaO₄.

Dopants	Formation Energy/f.u (eV)	ΔE_v (eV)	ΔE_c (eV)	Band gap (eV)
Pure BiTaO ₄	–	–	–	2.40
N _O	0.31	+0.28	0.01	2.13
N _O -N _O	0.63	+0.48	0.04	1.96
C _O	0.47	-0.07	-0.08	1.1
S _O	0.16	+0.09	-0.03	2.28
C _O -S _O	0.64	-0.04	-0.07	1.45

band. It is because of the N 2p orbital energy is higher than the O 2p orbital energy. VBM has been shifted 0.28 eV upward, CBM remains the same in its position. Shifting of the band edges are due to the doping of non-metallic elements in the system, which have been presented in Table 1. Overall band gap of single N-doped BiTaO₄ has been reduced by 11% as compared to the undoped system. VBM is comprised of N (p-state) and Bi (p-state) but N 2p is more prominent as compared to the others. The main contribution of the CBM is 5d Ta, which is not affected by this doping. The band gap narrowing would serve to contribute the enhancement of visible light absorption.

To study the dopant–dopant coupling, we have induced the two nitrogen atoms in the substitution of neighboring oxygen atoms, which are very close with distance, 2.79 Å. This gives almost the similar CBM as the undoped BiTaO₄. For this system, the VBM moves further in the upward direction, with empty band just above the Fermi level, which has contributed to the extra holes at the valence band as compared to the single nitrogen doping (shown in Fig. 3). In this case, band gap of the system has been reduced by 18% as compared to the pure BiTaO₄. The redox energy levels still lie in the band gap,

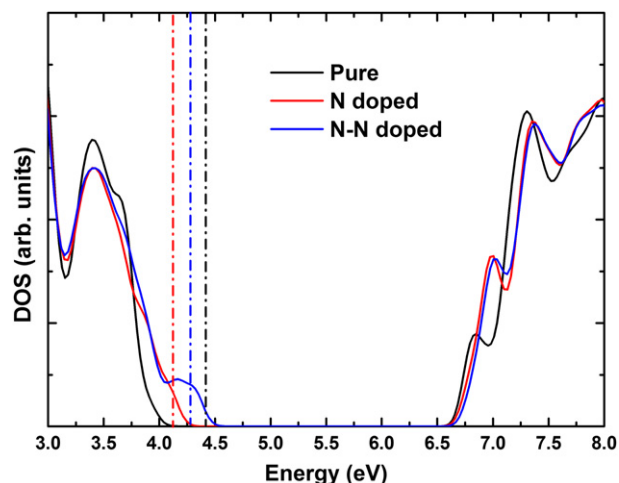


Fig. 3 – The calculated total density of states for N and N-N doped BiTaO₄ compared with the pure BiTaO₄; the DOSs for doped BiTaO₄ are shifted so that the peaks of the O 2s states (at the farthest site from the dopant) are aligned with each other. The vertical lines indicate the fermi levels.

which are important for hydrogen production. Holes mediated N-N coupling in BiTaO₄ is not short range coupling but N-N distance has been reduced by 0.22 Å after relaxation. Reduction in the band gap is larger than the individual N atom doping. To verify this N-N coupling, we have also studied dopant–dopant coupling with far distance (7.56 Å) in BiTaO₄. Total energy of the N-N doped BiTaO₄ with near configuration is 0.23 eV lower than far configuration. We have observed that the dopant–dopant coupling in far configuration has no effect on the band gap reduction and got the same band gap as in the case of single nitrogen doped system. The band gap of N_O and N_O-N_O doped BiTaO₄ are 2.13 and 1.96 eV, respectively, which are convenient for maximum utilization of the visible sunlight. It is also reduced the driving force for the oxidation process from 0.63 eV to 0.19 eV. We have been found that the N-N coupling in BiTaO₄ is very weak as compared to the TiO₂, which may be due to the N-N distance [21].

Let us consider S substitution with O, both S and O lie in the same column of the periodic table, sulfur element is just below the oxygen. One would expect that their electronic properties would not significantly change. The gap between the valence band and the conduction band is 2.28 eV, which is slightly less than the undoped BiTaO₄ gap. Doping of single sulfur atom in the BiTaO₄ does not have much effect on the VBM and CBM positions. But in the case of C doping in the system, the neutral 2p state of carbon is higher in energy than O 2p states. Therefore, double occupied (filled) states are developed and have situated deep inside the gap of BiTaO₄, which is shown in Fig. 4. These states are mainly composed of C 2p and Bi 6p, acts as double donor. The band gap of C-doped BiTaO₄ between the fully occupied states edge and CBM is only 1.1 eV. For the extraction of reasonable band gap between 1.1 and 2.28 eV, we have applied co-doping of C and S in the substitution of O in BiTaO₄, which may be more effective for the efficient photocatalyst material. In this case, the band gap of C-S co-doped BiTaO₄ has been reduced to 1.47 eV as compared to the pure BiTaO₄, which is suitable for the maximum utilization of the visible light spectrum but only reduction level lie in the band gap. It means that the oxidation

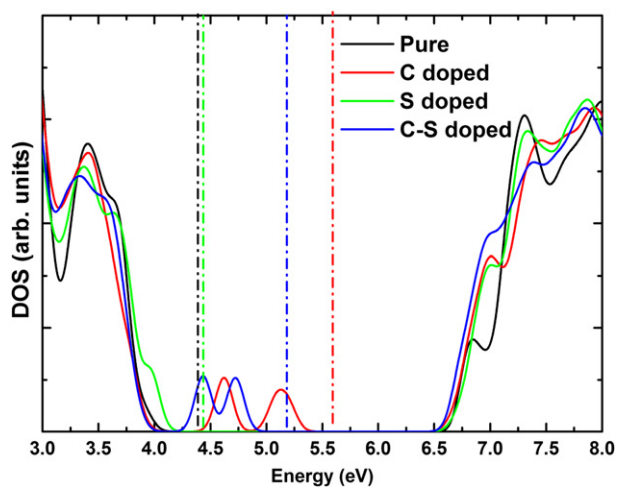


Fig. 4 – The calculated total density of states for C, S and C-S doped BiTaO₄ compared with the pure BiTaO₄; the vertical lines indicate the fermi levels.

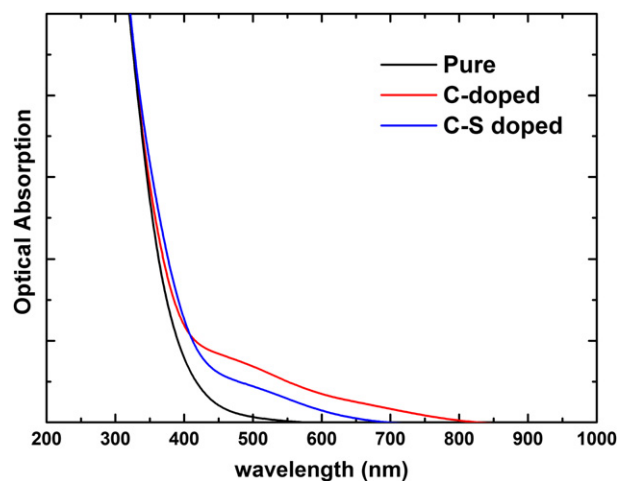


Fig. 5 – The calculated optical absorption spectrum of pure BiTaO₄ compared with mono- and co-doped BiTaO₄.

process is not possible in this system because the hole cannot spontaneously transfer to the oxidation potential. Total density of states (TDOS) are plotted by taking O 2s core states as reference, which are very far from the dopant and also indicates the Fermi levels by vertical lines (Fig. 4). If we compare this system with pure BiTaO₄ (shown in Fig. 2), oxidation level (O₂/H₂O) lie at the occupied levels, so oxidation is not possible in C and C-S doped BiTaO₄ but the reduction process (H⁺/H₂) is still energetically possible.

We have presented the optical absorption spectrum for C, and C-S doped BiTaO₄ and compared it with the pure bulk BiTaO₄, which is shown in Fig. 5. It is clearly observed that individual C has maximum narrowing the band gap as compared to others. C-S co-doping would lead to reasonable band gap reduction, which is very close to the required band gap for efficient photocatalytic material. To improve the photocatalyst efficiency of BiTaO₄ for water splitting, maximum absorption of solar visible light and driving force for the redox process are very important. For the doping of different non-metallic doping in the system, we need to shift the band edges or find some intermediate occupied states in the band gap. The occupied and unoccupied states in the band gap reduce the driving force for the transfer of holes for the oxidation process and increase the absorption of the visible light spectrum.

4. Conclusions

In summary, mono and co-doping of non-metallic elements is established for enhancing the visible-light photoactivity of BiTaO₄ by narrowing its band gap. First-principle calculations confirm that the band gap narrowing due to the N doping originates from mixing the O 2p and N 2p states in the VBM, which leads to move the valence band edge upward. Both the reduction and the oxidation process are energetically possible in the case of N or N-N doping in BiTaO₄. It has been observed that C-S co-doping reduce the band gap up to 39%, which is more favorable as compared to the single C or S. Shifting of

band edges play an important role to reduce required driving force for the redox process and absorbs the maximum visible sunlight, which are the main requirement of photocatalyst for the hydrogen production.

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REFERENCES

- [1] Lewis NS, Nocera DG. *Proc Nat Acad Sci* 2006;103:15729.
- [2] Eisenberg R, Nocera DG. *Inorg Chem* 2005;44:6799.
- [3] Fujishima A, Honda K. *Nature* 1972;238:37.
- [4] Licht S. *J Phys Chem B* 2001;105:6281.
- [5] Kudo A. *Int J Hydrogen Energy* 2006;31:197–202.
- [6] Walsh A, Yan Y, Huda MN, Al-Jassim MM, Wei S. *Chem Mater* 2009;21:547–51.
- [7] Tang J, Zou Z, Ye J. *Catal Lett* 2004;92:53.
- [8] Zou Z, Ye J, Sayama K, Arakawa H. *Chem Phys Lett* 2001;343:303–8.
- [9] Shi R, Lin J, Wang Y, Xu J, Zhu Y. *J Phys Chem C* 2010;114:6472–7.
- [10] Zou Z, Ye J, Arakawa H. *Int J Hydrogen Energy* 2003;28:663–9.
- [11] Bak T, Nowotny J, Cao Y, Yan W, Nowotny J, Rekas M, Sorrell CC. *Int J Hydrogen Energy* 2002;27:991.
- [12] Zang H, Chen G, Li X, Wang Q. *Int J Hydrogen Energy* 2009;34:3631–8.
- [13] Wang B, Li C, Hirabayashi D, Suzuki K. *Int J Hydrogen Energy* 2010;35:3306–12.
- [14] Gai Y, Li J, Li SS, Xia JB, Wei SH. *Phys Rev Lett* 2009;102:036402.
- [15] Xing C, Zhang Y, Yan W, Guo L. *Int J Hydrogen Energy* 2006;31:2018–24.
- [16] Luque A, Marti A. *Phys Rev Lett* 1997;78:5014.
- [17] Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y. *Science* 2001;293:269.
- [18] Huda MN, Yan Y, Moon C, Wei S, Al-Jassim MM. *Phys Rev B* 2008;77:195102.
- [19] Chen X, Burda C. *J Am Chem Soc* 2008;130:5018.
- [20] Mukherji A, Marschall R, Tanksale A, Sun C, Smith SS, Lu GQ, Wang L. *Adv Funct Mater* 2011;21:126–32.
- [21] Yin W, Wei S, Al-Jassim MM, Yan Y. *Phys Rev Lett* 2011;106:066801.
- [22] Nisar J, Wang BC, Pathak B, Kang TW, Ahuja R. *Appl Phys Lett* 2011;99:051909.
- [23] Chen X, Liu L, Yu PY, Mao SS. *Science* 2011;331:746.
- [24] Blochl PE. *Phys Rev B* 1994;50:17953.
- [25] Kresse G, Hafner J. *Phys Rev B* 1993;47:558.
- [26] Kresse G, Hafner J. *Phys Rev B* 1994;49:14251.
- [27] Kresse G, Hafner J. *Phys Rev B* 1999;59:1758.
- [28] Perdew JP, Chevary JA, Fiolhais C. *Phys Rev B* 1992;46:6671.
- [29] Monkhorst HJ, Pack JD. *Phys Rev B* 1976;13:5188.
- [30] Kajita S, Nakayama T, Yamauchi J. *J Phys Conf Ser* 2006;29:120–3.
- [31] Godby RW, Schluter M, Sham LJ. *Phys Rev Lett* 1986;56:2415.
- [32] Chakrapani V, Angus JC, Anderson AB, Wolter SD, Stoner BR, Sumanasekera GU. *Science* 2007;318:1424–30.
- [33] Weast RC, Astle MJ, Beyer WH. *Handbook of Physics and Chemistry*. 64th ed. CRC Press; 1983. D158.
- [34] Cui XY, Medvedeva JE, Delley B, Freeman AJ, Newman N, Stampfl C. *Phys Rev Lett* 2005;95:256404.
- [35] Zhao Z, Liu Q. *J Phys D Appl Phys* 2008;41:025105.