Study of electronic and optical properties of BiTaO$_4$ for photocatalysis

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We present the optical absorption spectrum of BiTaO$_4$ using the photo acoustic spectroscopy (PAS) technique and first principles approach. Band gap have been estimated 2.65 and 2.45 eV using PAS method and DFT calculations, respectively. Position of reduction and oxidation level with respect to vacuum level are identified, which shows that BiTaO$_4$ can be used as photocatalyst for hydrogen production. Electronic structure is explained by plotting total density of states (TDOS).

1 Introduction Photocatalytic materials have gained remarkable attention in the field of solar fuel production, which is a promising approach for the efficient solar energy conversion. This is an important step to implement a new energy matrix that is clean, environmentally friendly and independent of fossil reserves [1]. Many attractive semiconductor and oxide materials such as TiO$_2$, CdS, BiVO$_4$ and metal-free polymeric have been developed as photocatalyst for hydrogen production from water under visible light [2-4]. Electronic structure and optical properties of these materials are very crucial factors for the designing of photocatalyst and optoelectronic devices.

A suitable semiconductor photocatalyst for large scale solar hydrogen production must meet at the same time, at least, the following three requirements: (i) the band-gap energy must be 2.0 eV for efficient sun light absorption; (ii) the position of the valence band maximum (VBM) and the conduction band minimum (CBM) should match with the reduction and oxidation potential levels of water and (iii) it should be thermal and chemical stable in water environment. Reducing and oxidizing powers are measured by taking the energy difference between the redox potential levels and band edges [5], which are defined as $\Delta_1 = E_{CE} - E(H^+/H_2)$ and $\Delta_2 = E(H_2O/O_2) - E_{VE}$. Here, Δ_1

and Δ_2 are the reducing and oxidizing powers, respectively. Besides, band dispersion and high quality surface structure (low defect concentration) helps for high quantum efficiency [6] because defects generate donor or acceptor states in the band gap, which may be the cause of recombination of electrons and holes. Some metal species such as Pt, MoS$_2$ and RuO$_2$ [7, 8] could also be used as co-catalyst to move the photo induced charge carriers from the bulk to the surface of the material and increase the hydrogen production rate. Many alternative methods have been investigated to prepare these kind of materials, such as sol-gel citrate, co-precipitation [6-8], hydrothermal and combustion syntheses, which are advantageous in obtaining nanosized particles (hence high surface area), good homogeneity and lower energy consumption, because they operate in mild temperatures.

This paper reports on the optical properties of nanosized particles of BiTaO$_4$. Photo acoustic spectroscopy (PAS) technique was used to determine the band gap (E$_g$) at room temperature and compare these results with first principle calculations. We also investigate the electronic structure, optical properties and surface area of bulk and nanosized BiTaO$_4$.

2 Experimental procedures BiTaO$_4$ was prepared by the citrate method according to reference [9]. In a typical synthesis, bismuth citrate and tantalum pentachloride (TaCl$_5$) are used as starting materials and citric acid and ethylene glycol as chelating agent and reaction medium, respectively. The PAS experiments were performed using a spectrometer consisting of a 1000 W xenon arc lamp whose beam was modulated by a mechanical chopper (SRS, model SR540). This technique is able to give the absorption spectrum of a given sample directly [10]. The surface area was determined by BET (Brunauer, Emmett and Teller) measurements in a textural characteristics system by nitrogen adsorption (Micromeritics ASAP2020).

3 Computational details The first-principles calculations were performed using projected augmented wave (PAW) method [11] as implemented in the Vienna ab initio simulation package (VASP) [12]. The exchange-correlation interaction was treated in the level of the GGA using Perdew-Burke-Ernzerhof (GGA-PBE) [13]. We have employed a planewave basis set with an energy cutoff of 400 eV to describe the electronic wave function. In all calculations, self-consistency was achieved with a tolerance in the total energy of at least 0.1 meV.

4 Results and discussion X-ray diffraction (XRD) has been performed for the structure analysis of BiTaO$_4$. Figure 1 shows the XRD pattern of the powder calcined at 800 °C. At this temperature, the pure triclinic phase of BiTaO$_4$, known as high-temperature β-type is obtained which can be confirmed by comparison with the pattern (PDF 16-0906). The crystallite size of the samples can be estimated with the Scherrer's equation from XRD data:

$$D = \frac{0.89\lambda}{B\cos\theta},\qquad(1)$$

where λ is the X-ray wavelength of 1.541 Å, θ is the Bragg diffraction angle and B is the full width at half maximum (FWHM) of 2θ.
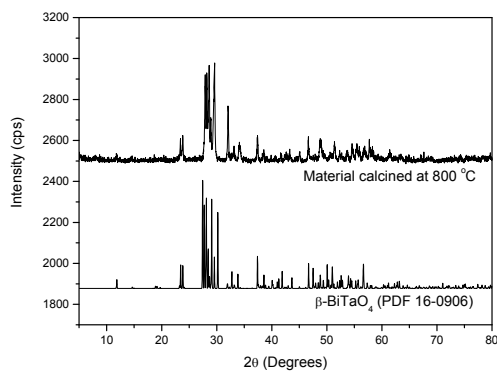
Crystallite size calculated was 47 nm. The citrate polymeric precursor method has proved efficient in the preparation of pure nanosized β-BiTaO$_4$ (triclinic system) at mild temperatures. While the solid state reaction method the pure phase of the oxide is obtained only at 1150 °C with the polymeric precursor method the same phase could be obtained at temperatures as low as 800 °C. Triclinic structure is confirmed by the atomic optimization of the system using DFT calculations. These calculations include optimization for both lattice parameters and coordinates of atoms for every configuration.

BET measurement showed that the surface area of triclinic BiTaO$_4$, obtained by polymeric precursor method at 800 °C for 3 hours, is 3.31 m^2 g^{-1}. This is much higher than BET surface area of the orthorhombic BiTaO$_4$, 0.49 m^2 g^{-1}, obtained by Zou *et al.* [14] when the oxide is synthesized by solid state reaction at 1100 °C for 48 hours. This means an enhancement of almost seven times in BET surface area of BiTaO$_4$ when it is obtained in mild temperatures. Since BiTaO$_4$ has demonstrated high activity as a photocatalyst in water splitting under UV light irradiation, it is evident that further increase in activity might be expected from increasing the surface area, because the photocatalytic reaction occurs in the surface of the oxide powder. To obtain the optical band gap energies, two different analytical methods were applied to the experimental data [10]. First, is the geometrical method, which uses the relation assuming transitions

$$I^n = A(h\nu - E_g),\qquad(2)$$

where E_g is the absorption intensity, A is a coefficient, $h\nu$ is the photon energy and n define the band transition. The value of E_g was obtained by extrapolation of the best linear fit between I and $h\nu$ up to the point where it crosses the ordinate axis; and second method is to evaluate the absorption intensity derivative near the fundamental absorption edge. The inflection point of the first derivative gives E_g.
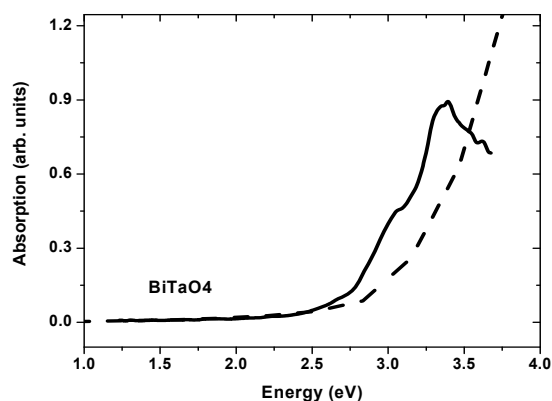

Figure 1 XRD pattern of the material calcined at 800 °C and ICSD pattern for the phase β-BiTaO$_4$.

Figure 2 Absorption spectra of β-BiTaO$_4$ as a function of photon energy, obtained by PAS and compared with DFT calculations. Experimental and theoretical results are indicated by full and dashed lines, respectively.

The energies for the direct and indirect gap transitions determined by geometrical and derivative methods through transmission for BiTaO₄ are summarized in Table 1. The total determination error of the energy gap is about 3%. The precision of our results is due to the large number of statistics, provided by long-term measuring routines. The errors derive from the absolute deviation of the measuring and the systematic deviation of optics, detectors and detection electronics. Figure 2 does not show sharp absorption edge for precise gap energies. The band gap of the BiTaO₄ is measured to be 2.52-2.79 eV by PAS method.

Table 1 Optical band gap of BiTaO₄ determined by geometrical, derivative and fitting methods.

Method		Band gap (eV)
$I^{1/2}$	Indirect gap	2.523 ± 0.065
I^2	Direct gap	2.687 ± 0.073
	Derivative	2.794 ± 0.075
	DFT	2.45
	Previous Exp.	2.7 [14]

We have studied the electronic structure of BiTaO₄ by first-principle approach and estimated the band gap energy. Electronic structure is explained by plotting total density of states (TDOS) which is shown in Fig. 3. It is known that the positions of the VBM and CBM are critical variable in determining the feasibility of solar driven hydrogen production. The calculated band gap of the BiTaO₄ is 2.4 eV with GGA-PBE, which is slightly under estimated the experimental band gap (see Table 1) due to the well-known LDA/GGA errors for semiconductors and insulators [15]. BiTaO₄ has enough band gap energy to overcome the endothermic characteristics (1.23 eV) of water splitting reactions [16].
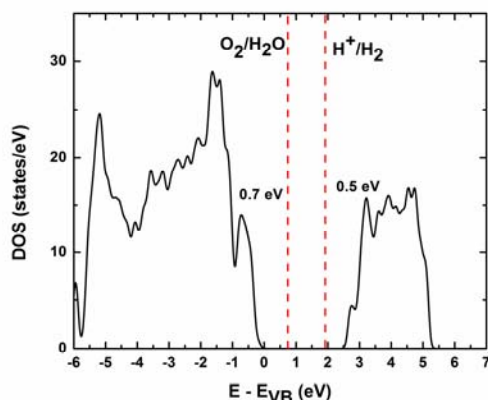

Figure 3 TDOS for bulk BiTaO₄. Reduction and oxidation potential levels with respect to band edges for water splitting.

Amount of energy equal to the band gap is required to transfer electrons from valence band to conduction band, so holes are generated in valence band. How-

ever, as displayed in Fig. 3, we compare the redox potential levels with respect to the band edges. Here we consider the situation of standard water redox potentials, which are -4.44 and -5.67 eV for reduction and oxidation process, respectively [16]. It shows that the energy level for water reduction (H^+/H_2) exist 0.5 eV lower than the CBM, thus leading to inject electrons into the solution phase for hydrogen production. Oxidation level (O_2/H_2O) exists about 0.7 eV higher the VBM, so the holes can spontaneously transfer to the oxidizing potential of the water splitting with oxidation power 0.7 eV. Reaction rate constant is defined by the Arrhenius equation; $C = Ae^{-E_a/RT}$, where C denotes the rate constant of the chemical reaction with the activation energy E_a, which are reducing or oxidizing power. Here. A, R and T are the constant factor, gas constant and the temperature. So we can get maximum efficiency of this water splitting process if oxidizing power is equal to the reducing power.

5 Summary We have investigated the electronic structure and optical properties of pure BiTaO₄ by the ab-initio calculations based on DFT and PAS method. Reduction and oxidation energy levels are aligned with respect to the VBM and CBM. Both the reduction and the oxidation process are energetically possible in BiTaO₄. The results highlight the possibility of developing the efficient photocatalyst for the hydrogen production from solar energy, which is very cheap and environmental friendly.

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