



Monoclinic bismuth vanadate band gap determination by photoelectrochemical spectroscopy



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HIGHLIGHTS

- Optical band gap of monoclinic BiVO₄ was determined by photocurrent spectroscopy.
- Indirect optical transitions are characterized by the energy $E_{gi} = 2.44$ eV.
- Direct optical transitions are characterized by the energy $E_{gd} = 2.63$ eV.

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ABSTRACT

The optical band gap (E_g) of the monoclinic bismuth vanadate BiVO₄ (scheelite) was determined by photoelectrochemical (photocurrent) spectroscopy. The relevance of this study is related to an existing ambiguity in E_g determination, which is due to possible distinction in preparation technique of this compound (and, hence, difference in grain size, crystallinity, film thickness, etc.), as well as realization of additional optical absorption mechanisms unrelated to excitation of electrons from the valence band to the conduction band. Using analysis of the Incident Photon-to-current Conversion Efficiency (IPCE), which minimizes a contribution of impurity-related and other kinds of absorption, it was demonstrated that BiVO₄ scheelite is primarily indirect band gap semiconductor, where indirect optical transitions are characterized by the energy gap $E_{gi} = 2.44$ eV, whereas for direct optical transitions energy gap is $E_{gd} = 2.63$ eV.

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1. Introduction

In the last decade the interest in optical properties of monoclinic bismuth vanadate has significantly increased due to its high activity in photocatalytic [1–7] and photoelectrochemical (PEC) [6–10] processes. An important advantage of monoclinic BiVO₄ over classical photocatalytic oxides (TiO₂, ZnO, WO₃) is its smaller band gap (E_g) which allows photoinduced processes under irradiation not only by UV but also by the visible part of the spectrum. E_g values of monoclinic BiVO₄ estimated from the long-wavelength edge of the diffuse reflectance spectra are in the range 2.33–2.50 eV [1,3,8,11]. The band gap for direct optical transitions (E_{gd}) calculated from the diffuse reflectance spectra using the Kubelka-Munk function by

some authors [5,6,12–14] was 2.45–2.46 eV, while higher values were reported by other authors: 2.48 eV [15], 2.52–2.56 eV [16], 2.60 eV [17], 2.68 eV [18]. The information concerning the values of indirect optical transitions band gap (E_{gi}) is more limited; in particular, according to G. Li et al. [19], E_{gi} value is 2.20 eV; O.F. Lopez et al. determined E_{gi} to be in the range from 2.35 to 2.42 eV [20], while from the results of P. Madhusudan et al. [4] E_{gi} values are 2.34 and 2.13 eV for polycrystalline and porous BiVO₄, respectively. Despite the fact that the vast majority of workers determined E_g values for the direct optical transitions, recently it has been proved conclusively that monoclinic BiVO₄ is indirect-gap semiconductor with E_{gi} value equal to 2.52 eV [18].

The ambiguity in determining the band gap values and optical transitions type in monoclinic BiVO₄ is not only due to the difference in the preparation technique (accordingly, differences in crystallite size, the ordering degree, film thickness, etc.), but also due to the presence of additional mechanisms of optical absorption

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without excitation of electrons from the valence band to the conduction band of semiconductor [21]. In particular, this kind of parasitic absorption in hydrogenated BiVO₄ was observed at a wavelength $\lambda > 530$ nm (photon energy $h\nu < 2.34$ eV) without contribution to photogeneration processes responsible for PEC activity of BiVO₄ photoanode [22].

Considering the foregoing discussion, in the present study the photocurrent spectroscopy has been used to determine the band gap of monoclinic BiVO₄. Photocurrent flows as a result of the generation of electron-hole pairs due to the interband absorption of photons with energy $h\nu \geq E_g$ with the subsequent involvement of the photogenerated charge carriers in a photoelectrochemical reactions. The advantage of this method of E_g determination in comparison with classical optical methods is the minimum impact of other absorption mechanisms besides the fundamental interband transitions in the photocurrent spectrum.

At the same time, the Incident Photon-to-current Conversion Efficiency (IPCE, Y) evaluated from photocurrent spectrum can be considered as $Y(\lambda) = Y_1(\lambda) \cdot Y_2(\lambda)$, where $Y_1(\lambda)$ is the fraction of incident photons resulted in electron-hole pair generation (proportional to the absorption coefficient near the absorption edge), and $Y_2(\lambda)$ is the fraction of the photogenerated charge carriers participating in photoelectrochemical reactions (determined by recombination losses, i.e. by relation between film thickness, diffusion length, surface recombination rate and depth of photocharges generation) [23]. It is obvious that spectral dependence of Y_2 can distort the obtained E_g value. Recently it has been shown that the photocurrent generated on BiVO₄ is not limited by surface reaction kinetics, but by surface recombination [24]. Therefore, to verify the correctness of E_g determination from IPCE spectra, it is necessary to compare results of E_g calculation obtained under different recombination impact. Such variation can be achieved by changing the film permeability for electrolyte, as well as photocharge generation depth. So, the films with different porosity have been studied and different geometries of their illumination have been used.

2. Experimental

BiVO₄ film electrodes were prepared by spin-coating (3000 rpm) of BiVO₄ colloidal solution on optically transparent substrate with a layer of electrically conductive fluorine-doped tin oxide (FTO). The colloidal solution was prepared by mixing of 0.75 mol/L Bi(NO₃)₃ and 0.075 mol/L of NH₄VO₃ aqueous solutions taken in a volume ratio of 1: 10 followed by centrifugation, 5 times washing with distilled water and ultrasonical dispersing (44 kHz, 10 min) with the addition of 30% aqueous ammonia solution (1:100 per volume) as a colloid stabilizer. To increase the porosity of BiVO₄ films, a 10% solution of polyvinyl alcohol (PVA) was added to BiVO₄ colloid in a ratio of 1:1 by volume. According to the adsorption analysis (Brunauer–Emmett–Teller method [25], N₂ adsorption at 77 K, ASAP 2020 surface area and porosity analyser, Micromeritics, USA), the addition of a pore-forming PVA increases the specific surface of the film from 3.2 to 5.8 m²/g and a specific pore volume from 0.006 to 0.011 cm³/g. Hereafter, the BiVO₄ films synthesized without and with PVA will be referred as “dense” and “porous”, respectively.

The heat treatment of prepared films in air at 450 °C for 2 h resulted in the formation of monoclinic crystal structure of BiVO₄ according to XRD and Raman spectroscopy (see below). From SEM results, the deposited BiVO₄ films were found to have a thickness of several hundred nanometers. These films are composed of rounded or elongated particles with a relatively small area of contact with each other (Fig. S1a). The addition of PVA to the suspension results in the subsequent partial fusion of BiVO₄ particles (Fig. S1b).

Despite such fusion of particles, the specific surface and pore volume increases by 1.8–2 times due to the formation of an additional porous during the thermal oxidation of PVA additive.

XRD patterns were taken in the Bragg–Brentano geometry with a Bruker D8 Advance diffractometer using Cu K α radiation. The average size (r) of crystallites was evaluated by the Scherrer formula from the half-width of the XRD peak corrected for the instrumental broadening: $r = 0.9\lambda_{K\alpha}/B_{2\theta}\cos\Theta$, where $\lambda_{K\alpha}$ is 0.15406 nm for copper anode, $B_{2\theta}$ is the full width at half-maximum of diffraction peak (2Θ scale, in radians).

Raman spectra were recorded at room temperature in the range of Raman shifts from 70 to 2400 cm⁻¹ using a Nanofinder HE confocal spectrometer (LOTIS TIL, Belarus – Japan) equipped with a solid-state laser ($\lambda = 532$ nm), 600 lines/mm grating (providing a spectral resolution better than 2.5 cm⁻¹) and a thermostated CCD camera.

Photocurrent spectra were obtained using a setup equipped with a MDR-23U high-intensity grating monochromator (spectral resolution 1 nm), a halogen lamp (250 W power, color temperature of 3350 K) and a light chopper (frequency of 0.3 s⁻¹). The potential of the semiconductor electrode was controlled by a P-8 potentiostat (Elins, Russia) equipped with a three-electrode quartz cell with a saturated silver chloride reference electrode (+0.201 V vs. SHE) and a platinum auxiliary electrode. 0.1 mol/L Na₂SO₃ aqueous solution was used as electrolyte, which is optically transparent in the BiVO₄ absorption area and can effectively scavenge the photogenerated holes. High electrical conductivity of the used solution (1.44 $\Omega^{-1}\text{m}^{-1}$ at 25 °C [26]) ensured insignificance of iR drop. IPCE was calculated from the photocurrent and the light intensity at the monochromator output measured by an OPT101P silicon photodiode (TI Burr-Brown, USA). Band-gap energies are presented as the mean value for the set of three individual samples. Standard deviation was calculated with statistical software of OriginPro 7.0 (OriginLab Corporation, USA).

Transmission and diffuse reflectance spectra were measured using an Agilent 8453 (Agilent Technologies, USA) and a Specord M40 (Carl Zeiss Jena, Germany) spectrometers, respectively, with spectral resolution about 1 nm.

3. Results and discussion

The identification of the crystal structure of the obtained BiVO₄ samples was carried out by comparison of their XRD patterns (Fig. 1a,c) and Raman spectra (Fig. 1b,d) with the literature [5,10,27–29].

XRD patterns of the grown films demonstrate only reflexes inherent to monoclinic scheelite-type BiVO₄. From broadening of XRD reflexes using the Scherrer equation, a grain size in the BiVO₄ films can be estimated as appr. 70 nm for “dense” and appr. 85 nm for “porous” films that exceeds significantly the Bohr radius of exciton, which is calculated to be equal to ≈ 9 nm (taking into account that $m_e = 0.9m_0$ and $m_h = 0.7m_0$ [30], $\epsilon = 68$ [31]). Thus, one can neglect electron quantum confinement effect on the IPCE spectra of the studied BiVO₄ films.

In the Raman spectra, the bands at 127 and 213 cm⁻¹ are associated with translational Ex_t and rotational Ex_r phonon vibration modes, at 325 and 367 cm⁻¹ – with asymmetrical δ_{as} and symmetrical δ_s bending vibrations in VO₄³⁻ tetrahedra, at 707 and 827 cm⁻¹ – with asymmetrical ν_{as} and symmetrical ν_s stretching vibrations in VO₄³⁻ tetrahedra in BiVO₄ monoclinic scheelite-type phase [5,10,27–29]. BiVO₄ films prepared using a pore-forming additive PVA have the similar spectral band positions.

Thus, XRD and Raman spectroscopy results demonstrate that BiVO₄ films used in this study have the scheelite-type monoclinic crystal structure regardless of their porosity. It should be noted that

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