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Phase relations and optoelectronic characteristics in the $NdVO_4$–$BiVO_4$ system

Mirela Dragomir [a,*], Iztok Arčon [a,b,c], Sandra Gardonio [a], Matjaz Valant [a,d]

[a] University of Nova Gorica, 5000 Nova Gorica, Slovenia
[b] Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
[c] CO-NOT, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
[d] Center of Excellence for Biosensors, Instrumentation and Process Control, 5250 Solkan, Slovenia

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Abstract

Studies performed on the $NdVO_4$–$BiVO_4$ system showed the existence of the $Bi_xNd_{1-x}VO_4$ homogeneity range for $x \leqslant 0.49(1)$. Extended X-ray absorption fine structure and X-ray diffraction analyses confirmed that Bi^{3+} is incorporated onto the Nd site in the $NdVO_4$ crystal structure with some distortion of the local structure. Surprisingly, the unit cell volume decreases with the increase in the content of the larger Bi^{3+} ion. On the other side of the $NdVO_4$–$BiVO_4$ system, Nd^{3+} does not enter the $BiVO_4$ structure but forms the $NdVO_4$-based secondary phase. Ultraviolet–visible spectroscopy showed that the band gap of $NdVO_4$ can be reduced to below 3.1 eV by the Bi doping. New emissions that do not exist for $NdVO_4$ have been found in the 650–675 nm range of $Bi_xNd_{1-x}VO_4$ photoluminescence spectra. The observed chemical and optoelectronic properties were explained on the basis of the hybridization of Bi $6s^2$ and O $2p$ orbitals.

Keywords: Photocatalysis; Orthovanadates; Solid solution; Extended X-ray absorption fine structure; Optical spectroscopy

1. Introduction

Efficient use of solar energy still remains a challenge due to the lack of a stable and efficient visible-light-active photocatalyst [1,2]. Most of the photocatalytic materials developed so far are wide-band-gap semiconductors (e.g. TiO_2, $SrTiO_3$, WO_3) active only under ultraviolet (UV) light [3–6]. For an effective use of sunlight, several different techniques for tuning their optoelectronic properties towards the visible spectral range have been developed, e.g. band gap engineering by doping [2,7], use of co-catalysts [8] and sensitizers [9] etc. Another approach is the development of new, more effective, narrow-band-gap semiconducting materials.

Monoclinic $BiVO_4$ (with a distorted scheelite structure, space group $I2/b$, also called fergusonite) has been recognized to be an efficient, chemically stable, visible-light-active photocatalytic material [10,11]. Two other polymorphs of $BiVO_4$ are known: tetragonal dreyerite (zircon-type structure, space group $I4_1/amd$) and tetragonal scheelite (space group $I4_1/a$). The monoclinic scheelite-type phase undergoes a reversible second-order transition to the tetragonal scheelite structure at ∼528 K [12–14]. This phase transition has been found to be driven by a small lone pair distortion on the Bi^{3+} ion [13]. A metastable tetragonal zircon-type $BiVO_4$ phase undergoes an irreversible transformation to the monoclinic scheelite-type on heating at 670–770 K [14], or by mechanical stress [12]. The different $BiVO_4$ polymorphs have different absorption characteristics and, consequently, their photocatalytic activities differ significantly. For instance, the tetragonal $BiVO_4$ with a band gap of 2.9 eV shows the absorption band in the near UV [15], while the monoclinic form with a band gap of 2.4 eV shows the absorption band in the visible region [15–17]. $BiVO_4$ in the monoclinic form is a well-known chemically stable and nontoxic visible-light photocatalyst

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* Corresponding author. Tel.: +386 5 365 35 39; fax: +386 5 365 35 27.
E-mail address: mirela.dragomir@ung.si (M. Dragomir).

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with an excellent photocatalytic activity that is attributed to its narrow band gap and large bandwidths [18]. In conventional metal oxide semiconductors, the top of the valence band is solely contributed by O 2*p* orbitals, resulting in a wide band gap, but in the case of the monoclinic $BiVO_4$, the Bi $6s^2$ lone pair electrons create hybridized orbitals with O 2*p* orbitals [19,20], which leads to an up-shift of the top of the valence band, while the bottom of the conduction band remains unaffected due to its V 3*d* nature. Furthermore, the low effective mass of electrons and holes [18–20] and high energy dispersion in the band structure of $BiVO_4$ [18] significantly improve separation and transport properties of the photoexcited charges. $BiVO_4$ is known to be a good photocatalyst for the degradation of organic dyes [11,21] and a stable oxygen evolution catalyst in the presence of sacrificial electron acceptors (such as Ag^+) [10,21]. But it is catalytically inactive for hydrogen evolution due to its too low conduction band position relative to the proton reduction potential. Even though $BiVO_4$ has an unsuitable band position for hydrogen evolution, the overall water splitting reaction can still be achieved by using a separate hydrogen evolution catalyst in tandem (Z-scheme) [22]. Although the monoclinic $BiVO_4$ exhibits very interesting optoelectronic properties, its photocatalytic activity is still low. A shape-controlled synthesis of $BiVO_4$ particles has been proven to be an efficient way to increase its photocatalytic activity [11,21,23]. Another way to enhance the photocatalytic performance of $BiVO_4$ is by doping or metal loading. Loading with noble metals such as Pt [24], Pd [25], Au [26] or Ag [27] or with transitional metals, such as Co [27–29], Ni [27], Fe [30] or Cu [31], increased the photocatalytic activity of $BiVO_4$ by reducing the electron–hole recombination rate due to a better electron–hole separation near the metal–semiconductor junctions. A moderate B-site doping with Mo [32], W [33] or P [17] can improve the electron transport in $BiVO_4$, while a recent study [34] reported that doping of $BiVO_4$ with Al is another efficient way to suppress the recombination of the excitons. No successful A-site doping of the monoclinic $BiVO_4$ has been reported so far with the exception of co-substitution of Bi and V with Ca and Mo [16], respectively, which converted the monoclinic unit cell to tetragonal. The isovalent A-site substitutions with rare-earth ions such as Ce [35], Eu [36,37], Gd [36], 8 at.% Nd [36] and Er [36,38] have not been successful. An XPS analysis has shown segregation of Eu_2O_3 and Gd_2O_3 on the surface of the monoclinic $BiVO_4$ particles, which has been the reason for the observed enhanced photocatalytic activity.

It has recently been found that $NdVO_4$ (a wide-band-gap semiconductor with a zircon-type structure and $I4_1/amd$ space group [39]) exhibits a photocatalytic activity for degradation of dyes and organic pollutants which is comparable [40] or even higher than that of the commercial TiO_2 [41]. But due to its wide band gap (>3 eV), $NdVO_4$ is a UV active material [42]. Reports on the doping of $NdVO_4$ have shown that the photocatalytic activity of $NdVO_4$ under UV and visible-light (UV–vis) irradiation can be improved by B-site Mo doping [43]. Such doping reduces the band gap and broadens the distribution of the density of states in the conduction band. However, the synthesis of Bi-doped $NdVO_4$ and the effect of Bi doping on the structure and, consequently, on the electronic properties of neodymium orthovanadate have not yet been reported.

The aim of this study is to investigate phase relations and solid solution formation in the $NdVO_4$–$BiVO_4$ system and characterize the crystal structure and optoelectronic properties of the existing phases with X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS), diffuse reflectance (DRS) and photoluminescence (PL) spectroscopy techniques. For the solid solution between $NdVO_4$ and $BiVO_4$ we can expect a reduction in the band gap of $NdVO_4$ through coupling between Bi $6s^2$ and O 2*p* orbitals, which would move the absorption towards the visible-light range and contribute to a higher photocatalytic activity. To optimize this bad gap modification, the substitution mechanisms and the extent of the homogeneity ranges have to be determined.

2. Experimental section

Bi-doped $NdVO_4$ with a nominal stoichiometry of $Bi_xNd_{1-x}VO_4$ ($x = 0$, 0.10, 0.40, 0.45, 0.48, 0.50 and 0.60) and Nd-doped $BiVO_4$ with a nominal stoichiometry of $Nd_yBi_{1-y}VO_4$ ($y = 0$, 0.05, 0.08, and 0.10) were prepared by the solid-state method. Stoichiometric amounts of Bi_2O_3 (Alfa Aesar, 99.975% purity), V_2O_5 (Alfa Aesar, 99.6% purity) and Nd_2O_3 (Alfa Aesar, 99.6% purity) were homogenized in a planetary mill using ethanol as a homogenizing medium. The powders were dried and pressed into pellets. The $Bi_xNd_{1-x}VO_4$ samples were calcinated in air in two steps, at 973 K for 3 h and 1073 K for 3 h. The $Nd_yBi_{1-y}VO_4$ samples were fired in air at 1073 K for 10 h.

The crystallographic characterization was carried out with X-ray powder diffraction using a PANalytical X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm), a step size of 0.017° and scan step time of 25.8 s. The diffraction patterns were recorded in the range $2\theta = 5$–80°. Crystallite size calculation and the refinement of the unit cell were performed using the PANalytical X'pert High Score Plus software.

Bi L_3-edge Nd L_3-edge and V K-edge EXAFS spectra were measured at C beamline of HASYLAB (Hamburg, Germany) in a transmission detection mode at room temperature, using a Si(3 1 1) double-crystal monochromator with ~1.5 eV resolution at the Bi L_3-edge (13419 eV), and Si(1 1 1) double-crystal monochromator with 1 eV resolution at the Nd L_3-edge (6208 eV) and V K-edge (5465 eV). The higher-order harmonics were efficiently eliminated by detuning the monochromator crystals to 60% of the rocking curve maximum using a stabilization feedback control. The intensity of the X-ray beam was measured by three consecutive 10 cm long ionization detectors, the first filled with 190 mbar of Ar, and the second and third with 1000 mbar of Kr, for the Bi L_3-edge EXAFS, while for the Nd L_3-edge and V K-edge EXAFS