**Phase relations and optoelectronic characteristics in the NdVO4-BiVO4 system**

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**Abstract**

Studies performed on NdVO4-BiVO4 system showed on existence of the Bi*x*Nd1*−x*VO4 homogeneity range for x ≤ 0.49(1). EXAFS and XRD analyses confirmed that Bi3+ incorporates onto the Nd site in the NdVO4 crystal structure with some distortion of the local structure. Surprisingly, the unit cell volume decreases with the increase in the content of the larger Bi3+ ion. On the other side of the NdVO4-BiVO4 system, Nd3+ does not enter the BiVO4 structure but forms the NdVO4-based secondary phase. UV-Vis spectroscopy showed that the band gap of NdVO4 can be reduced to below 3.1 eV by the Bi-doping. New emissions that do not exist for NdVO4 have been found in the 650-675 nm range of Bi*x*Nd1*−x*VO4 photoluminescence spectra. The observed chemical and optoelectronic properties were explained on the basis of the hybridization of Bi6s2 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 photocatalytic materials, developed so far, are wide-band gap semiconductors (e.g. TiO2, SrTiO3, WO3 etc) 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 development of new, more effective, narrow-band gap semiconducting materials.

Monoclinic BiVO4 (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 BiVO4 are known: tetragonal dreyerite (zircon-type structure, space group I41/amd) and tetragonal scheelite (space group I41/a). The monoclinic scheelite-type phase undergoes a reversible second-order transition to the tetragonal scheelite structure at about 528 K [[12](file:///C:\Users\mvalant\AppData\Article_Mirela\References%20article%201\Phase%20transition%20in%20BiVO4.pdf)-14]. This phase transition has been found to be driven by a small lone pair distortion on the Bi3+ ion [13]. A metastable tetragonal zircon-type BiVO4 phase undergoes an irreversible transformation to the monoclinic scheelite-type on heating at 670–770 K [14], or by mechanical stress [12]. The different BiVO4 polymorphs have different absorption characteristics and, consequently, their photocatalytic activities differ significantly. For instance, the tetragonal BiVO4 with a band gap of 2.9 eV shows the absorption band in the near UV [[15]](file:///C:\Users\mvalant\AppData\Article_Mirela\References%20article%201\mirela4.pdf), while the monoclinic form with a band gap of 2.4 eV shows the absorption band in the visible region [15–17]. BiVO4 in the monoclinic form is a well-known chemically stable and nontoxic visible-light photocatalyst 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 2p orbitals resulting in a wide band gap, but in the case of the monoclinic BiVO4, the Bi 6s2 lone pair electrons create hybridized orbitals with O 2p 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 3d nature. Furthermore, the low effective mass of electrons and holes [18–20] and high energy dispersion in the band structure of BiVO4 [18] significantly improve separation and transport properties of the photoexcited charges. BiVO4 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 BiVO4 has the 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 BiVO4 exhibits very interesting optoelectronic properties, its photocatalytic activity is still low. A shaped-controlled synthesis of BiVO4 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 BiVO4 is by doping or metal loading. Loading with noble metals such as Pt [24], Pd [25], Au [26], Ag [27] or with transitional metals, such as Co [27–29], Ni [27], Fe [30] or Cu [31], increased the photocatalytic activity of BiVO4 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](file:///C:\Users\mvalant\AppData\Article_Mirela\References%20article%201\Mo-BiVO4.pdf)], W [33] or P [17] can improve the electron transport in BiVO4, while a recent study [[34](file:///C:\Users\mvalant\AppData\Article_Mirela\References%20article%201\Al-BiVO4.pdf)] reported that doping of BiVO4 with Al is another efficient way to suppress the recombination of the excitons. No successful A-site doping of the monoclinic BiVO4 has been reported so far with an 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-earths ions such as Ce [[35](file:///C:\WINDOWS\Temp\References%20article%201\cerium%20doped%20BiVO4.pdf)], Eu [36,37], Gd [36], 8 at.% Nd [36], and Er [36,38] have not been successful. An XPS analysis has shown segregation of Eu2O3 and Gd2O3 on the surface of the monoclinic BiVO4 particles, which has been the reason for the observed enhanced photocatalytic activity.

It has recently it been found that NdVO4 (a wide band gap semiconductor with a zircon-type structure and I41/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 TiO2 [41]. But due to its wide band gap (>3eV), NdVO4 is an UV active material [42]. Reports on the doping of NdVO4 have showed that the photocatalytic activity of NdVO4 under UV and visible-light 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 NdVO4 and the effect of Bi-doping on the structure and, consequently, on the electronic properties of neodymium orthovanadate has not yet been reported.

The aim of this study is to investigate phase relations and solid solution formation in the NdVO4-BiVO4 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 NdVO4 and BiVO4 we can expect a reduction in the band gap of NdVO4 through coupling between Bi 6s2 and O 2p orbitals, which would move the absorption towards the visible-light range and contribute to the 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 NdVO4 with a nominal stoichiometry of Bi*x*Nd1*−x*VO4 (x = 0, 0.10, 0.40, 0.45, 0.48, 0.50, and 0.60) and Nd-doped BiVO4 with a nominal stoichiometry of Nd*y*Bi1*−y*VO4 (y = 0, 0.05, 0.08, and 0.10) were prepared by the solid-state method. Stoichiometric amounts of Bi2O3 (Alfa Aesar, 99.975% purity), V2O5 (Alfa Aesar, 99.6% purity) and Nd2O3 (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*x*Nd1*−x*VO4 samples were calcinated in air in two steps, at 973 K for 3 h and 1073 K for 3 h. The Nd*y*Bi1*−y*VO4 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 K*α* radiation (λ = 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*θ* = 5-80°. Crystallite size calculation and the refinement of the unit cell were performed using the PANalytical X’pert HighScore Plus software.

Bi L3-edge Nd L3-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(311) double-crystal monochromator with ~1.5 eV resolution at the Bi L3-edge (13419 eV), and Si(111) double-crystal monochromator with 1 eV resolution at the Nd L3-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 L3-edge EXAFS, while for the Nd L3-edge and V K-edge EXAFS the cells were filled with 520 mbar of N2, 250 mbar of Ar, and 400 mbar of Ar, respectively. The samples were placed between the first two detectors. The exact energy calibration was obtained by an absorption measurement on Pb metal foil (Pb L3-edge 13035 eV), or Bi metal foil and Ti metal foil (Ti K-edge 4966 eV) or V metal foil, inserted between the second and the third ionization detector. The samples were prepared in the form of homogeneous pellets with an absorption thickness of about 2 above the investigated absorption edge, prepared from micronized powder homogeneously mixed with micronized BN powder. The absorption spectra were measured within the interval from -250 eV to 1000 eV relative to the absorption edge. In the edge region the equidistant energy steps of 0.3 eV were used, while for the EXAFS region the equidistant k-steps (Δk ≈ 0.03 Å-1) were used with an integration time of 1 s/step. The EXAFS spectra were further analysed with the IFEFFIT program package [44].

To obtain the band gap excitation profiles and the band gap energies, diffuse reflectance spectra were recorded in the range from 250 to 800 nm with a UV-Vis spectrophotometer (Perkin Elmer, model *λ* 650S) equipped with a 150 mm integrated sphere and using spectralon as a reference material. According to the Kubelka-Munk theory [45], the diffuse reflectance data were converted to absorbance coefficients *F(R∞)*. *F(R∞)* = *(1-R)2/2R* = *K/S*, where *R*, *K* and *S* are the reflectance, effective absorption and scattering, respectively. The band gap (*Eg*) energies and absorption coefficients are related through the following relation [46]: *αhν = A(hν - Eg)n/2*, where *α,* *hν* and *A* are linear absorption coefficient, photon energy and proportionality constant, respectively. *n* = 1 for a direct band gap semiconductor or 4 for an indirect band gap semiconductor. Both NdVO4 and BiVO4 are direct band gap semiconductors so *n =* 1. Plotting the *[F(R∞)hν]1/n* against excitation energy allowed us to evaluate the band gap energy (the extrapolation of the linear part of the absorption edge on the photon energy axis gives the band gap energy).

Photoluminescence (PL) emission spectra are useful in determining the efficiency of charge carrier trapping, the migration and transfer, as well as in understanding the evolution of electron-hole pairs in semiconductors. The PL spectra were taken with a FLS920 Spectrometer of Edinburgh Instruments, using a steady state Xenon arc lamp. The experimental set-up was equipped with a blue sensitive high speed photomultiplier (Hamamatsu H5773-03 detector). The emission spectra were collected at room temperature, within 400-700 nm with an excitation wavelength of 371 nm.

**3. Results and discussion**

3.1. Structural analysis

3.1.1. X-ray powder diffraction

The XRD patterns in Fig. 1 show the formation of tetragonal Bi*x*Nd1*−x* VO4 solid solution for x between 0 and 0.48. When x > 0.48, two phase mixtures were obtained, which contained tetragonal Bi*x*Nd1*−x*VO4 and monoclinic BiVO4. This shows that the solubility limit of Bi in NdVO4 is between x=0.48 and 0.50. The crystallographic details of the Bi*x*Nd1*−x*VO4 samples, obtained after refinement of the unit cell, are presented in Fig. 2. The standard deviation of the calculated unit cell parameters was ± 0.0002 Å. As the composition of the solid solution changes, the lattice constant also changes. We observed that the NdVO4 unit cell volume decreased according to Vegard’s law with the dopant concentration up to x = 0.48, while for higher concentrations, the unit cell volume remained constant. Thus, the solid solubility limit was found to be at x = 0.49(1).

The XRD patterns of Nd*y*Bi1*−y*VO4 (y < 0.08) compositions in Fig. 3 show the presence of only monoclinic BiVO4 phase. For y ≥ 0.08, additional peaks of the tetragonal NdVO4-based structure appear in the XRD pattern. The unit cell volume of this structure corresponds to the end member of the BixNd1-xVO4 solid solution with x = 0.49(1). Because of very small dopant concentration and limited sensitivity of the XRD technique, we could not make convincing conclusions about the Nd substitution in BiVO4 even for the y < 0.08 samples that appear to be single phase. Therefore, we have performed EXAFS studies to verify whether or not Nd3+, in small concentrations enters the crystal structure of BiVO4.

3.1.2. EXAFS study

3.1.2.1. Bi-doped NdVO4

The XRD analysis on the Bi-doped NdVO4 sample with Bi0.2Nd0.8VO4 composition only showed the presence of tetragonal NdVO4-based structure (space group I41/amd). To study distortion of the NdVO4 local structure with the Bi-doping, we used EXAFS analysis–a chemically selective method that enables to study the crystallographic environment around Bi ions. Distinctive peaks in the Fourier transforms (FT) magnitude of the EXAFS spectra are contributions of the photoelectron backscattering on the near neighbor shells around the central atom and represent the approximate radial distribution of the atoms surrounding the investigated central atom. The FT magnitude of k2-weighted EXAFS spectra for Nd, Bi and V that were calculated over the range of k = 4–11 A-1 are compared in Fig. 4. Errors in FT magnitude EXAFS spectra due to the random noise in χ(k) are estimated at high R values (in the interval from 8–15 Å) and are of the order of ± 6·10-3 for the Bi, ± 2·10-2 for the Nd, and ± 4·10-2 for the V spectrum. The qualitative comparison between the measured EXAFS signals shows that the Bi spectrum exhibits similar distribution of neighbour peaks as the Nd spectrum, and significantly different from the V one, suggesting that Bi ions in Bi0.2Nd0.8VO4 have similar environment as Nd ions in NdVO4. Such result was expected because the ionic radius of Bi3+ (1.17 Å) is similar to that of Nd3+ (1.11 Å), and much larger than that of V5+ (0.54 Å) [47]. It is therefore most unlikely that Bi3+ would replace V5+ in the NdVO4 crystal lattice. The quantitative structural information on the local Bi neighbourhood in Bi0.2Nd0.8VO4 and of Nd in NdVO4 (type and average number of neighbour atoms and their distances from the selected atom, as well as the thermal or structural disorder of their positions - Debye-Waller factors) was obtained by Bi L3-edge and Nd L3-edge EXAFS analysis in which the model EXAFS function was fitted to the measured EXAFS spectrum. For that purpose we used FEFF6 computer code [48] to construct Nd model EXAFS functions *ab initio* from a set of scattering paths of the photoelectron, built from crystallographic data for NdVO4 with I41/amd space group (a = b = 7.33Å, c = 6.43 Å, α = β = γ = 90º [49]. In this crystal structure, the Nd atoms are surrounded by eight O atoms, four at the distance of 2.36 Å, and four at 2.64 Å. The second coordination sphere is occupied by two V atoms at 3.21 Å, followed by four V and four Nd atoms at 4.00 Å, and twelve O atoms at 4.4 Å.The Bi EXAFS model is constructed from the same crystal structure with introduction of Bi on the Nd crystallographic site. All single and multiple scattering paths in the R range up to 4.09 Å were included in the models; in total 4 single scattering and 6 multiple scattering paths. A minimum number of variable parameters were introduced in the fits: a separate Debye-Waller factor (*σ2*) and a common relative change of distances (*ΔR/R*) for each shell of neighbours, except for the first shell where a separate *ΔR* was used. The common shift of the energy origin, *ΔE0*, and the common amplitude reduction factor, *S02*, were allowed to vary. In both models, the shell coordination numbers (*N*) were kept fixed at crystallographic values. The best-fit parameters are given in Table 1, and the quality of the fit is illustrated in Fig. 5 A and B. The error due to the random noise in χ(k) is ± 0.5·10-4 and ± 1 10-3 for Bi and Nd spectrum, respectively. Errors in FT magnitude EXAFS spectra due to the random noise in χ(k) are estimated at high R values (in the interval from 8–15 Å) and are of the order of ± 6·10-3 for Bi and ± 2·10-2 for Nd spectrum. From the results of the Bi and Nd EXAFS analysis, we observed that the Bi neighbourhood in Bi0.2Nd0.8VO4 is almost identical to that of Nd in NdVO4. Only a small decrease (~2%) in the closest neighbour distances was found for Bi ions. These findings are consistent with the XRD study (see section 3.1.1) that showed a decrease in the unit cell volume of Bi*x*Nd1*-x*VO4 with Bi concentration. The smaller unit cell of Bi*x*Nd1*-x*VO4 as compared to NdVO4 could be a consequence of the incorporation of Bi3+cation with a stereochemically active lone electron pair.

3.1.2.2. Nd – doped BiVO4

The XRD pattern of the sample with the nominal composition Nd0.05Bi0.95VO4 corresponds to the single-phase monoclinic BiVO4.We used the EXAFS analysis to determine whether Nd has indeed entered the crystal structure of BiVO4. We measured Nd L3-edge EXAFS on the sample with the nominal composition Nd0.05Bi0.95VO4, and V K-edge and Bi L3-edge EXAFS on BiVO4 sample. The FT of k2-weighted Nd, Bi and V EXAFS spectra were calculated over the range of k = 3.5–10.5 Å-1 Errors in FT magnitude EXAFS spectra due to the random noise in χ(k) are estimated at high R values (in the interval from 8–15 Å) and are of the order of ± 1·10-3 for the Bi, ± 1·10-2 for the Nd, and ± 3·10-3 for the V spectrum.

The comparison between the measured FT EXAFS signals (Fig. 6) shows significant differences between the three spectra. Neither Bi nor V spectrum is similar to the Nd spectrum. This comparison strongly suggests that Nd in the sample with the nominal composition Nd0.05Bi0.95VO4 does not have the same environment as Bi or V in BiVO4. Therefore, Nd is probably forming a secondary phase with different local structure. Based on the described XRD studies it is reasonable to assume that the secondary phase is the Bi*x*Nd1*-x*VO4 end member, i.e. Bi0.49Nd0.51VO4.

In order to fit the Nd EXAFS spectrum, we constructed Nd model EXAFS functions *ab initio,* from crystallographic data of the NdVO4 reference [49], as described in the previous section (3.1.2), but in this case we substituted 50% of Nd neighbour atoms with Bi atoms, to obtain the EXAFS model for the Bi0.5Nd0.5VO4 crystal structure. In the EXAFS model function all single and multiple scattering paths in the R range up to 5.1 Å were included. A minimum number of variable parameters were introduced in the fit: a separate Debye-Waller factor (*σ2*) and a common relative change of distances (*ΔR/R*), for each shell of neighbours, except for the first Nd-O distance and for the Nd-Bi distance where separate *ΔR* were used. The common shift of the energy origin, *ΔE0*,and the common amplitude reduction factor *S02* were allowed to vary. The shell coordination numbers (*N*) were kept fixed at the crystallographic values of the model Bi0.5Nd0.5VO4 structure.

A very good fit of the experimental spectrum with the model Bi0.5Nd0.5VO4 structure was obtained for the fitting performed in the *k* range from 3.4 Å-1 to 10 Å-1, and the *R* range from 1.35 Å to 5.1 Å. A complete list of the best-fit parameters is given in Table 2, and the quality of the fit is illustrated in Fig. 7. The error due to the random noise in χ(k) is ± 4·10-3; and the error in FT magnitude EXAFS spectrum due to the random noise in χ(k) is estimated at high R values and is of the order of ± 1·10-2.

From the parameters of the fit we can see that the local structure around Nd atoms in the sample with the nominal Nd0.05Bi0.95VO4 composition is very similar to the local structure of Nd in NdVO4 (see Table 1). However, we found that the Bi atoms are located at 0.3 Å larger distances as Nd atoms from the same shell. Also the distances to the oxygen atoms in more distant coordination shells are not the same as in the undoped NdVO4, which indicates on some degree of structural distortion induced by the incorporation of Bi.

The results of the EXAFS analysis show that even for the smallest concentrations, Nd did not enter the crystal structure of BiVO4 but it formed, most probably nanocrystalline, secondary BixNd1-xVO4 phase with x = 0.49(1). The fact that Nd did not enter the BiVO4 crystal structure is somewhat surprising, taking into account that the ionic radii of Nd3+ and Bi3+are very similar (1.11 Å and 1.17 Å, respectively). The result indicates that for the stabilization of the BiVO4 structure, the specific electron structure of Bi3+ is crucial. It appears that the hybridization of the Bi 6s2 and O 2p orbitals stabilizes the monoclinic BiVO4 structure by distorting the Bi cation environment and adjusting the oxygen coordination sphere correspondingly. The distance of the A-site ion to the first oxygen coordination sphere is shorter in the monoclinic BiVO4 than in the tetragonal NdVO4 (2.35 Å [[50](file:///C:\Users\mvalant\AppData\Article_Mirela\References%20article%201\CRYSTAL%20GROWTH%20AND%20STRUCTURE%20OF%20BiVO%204.pdf)] and 2.44 Å, respectively) and, therefore, such cation site cannot be occupied by Nd3+ ion without the ability for the hybridization. This also explains why NdVO4 and BiVO4 crystallize in very different crystal structures and no Nd3+ can enter the A-site of BiVO4. For the same reason no successful substitution on the A-site of the monoclinic BiVO4 has been reported so far. NdVO4 can adopt the monoclinic BiVO4-type of structure but only under high pressure [[39](file:///C:\Users\mvalant\AppData\Article_Mirela\References%20article%201\The%20electronic%20structure%20of%20zircon-type%20orthovanadates%20Effects%20of.pdf)]. Such monoclinic structure with rare earth ions on the A-site is a metastable polymorph, in which, instead of the hybridization, the cation-oxygen distances are reduced by application of the external pressure.

3.2. Optoelectronic properties

3.2.1. Band gap analysis

The diffuse reflectance spectra of Bi*x*Nd1*−x*VO4 powders after the Kubelka-Munk treatment are presented in Fig. 8. The band gap of the single phase NdVO4 was calculated to be 3.53 eV. This value is in the range of values reported in the literature (see Table 3), which significantly differ according to the morphology of the samples. From the Table 3 we can see a strong correlation of the particle size and the band gap values; smaller the particle size, smaller the band gap. Our result fits well into this trend. With introduction of Bi onto the A-site of NdVO4, the band gap decreases from initial 3.53 eV to 3.06 eV for y = 0.40. In the lower concentration range, the influence of Bi on the band gap reduction is strong but becomes weaker for x ≥ 0.20.

Taking in consideration the band structure of BiVO4 and NdVO4 [19,20,39], the observed red-shift of the Bi*x*Nd1*-x*VO4 band gap could be ascribed to the hybridization between Bi 6s2 and O 2p orbitals on the top of the valence band of NdVO4,which results in the up-shift of the valence band. This can be correlated with the colour change that we observed upon Bi doping, from blue-grey of NdVO4 towards more yellowish green for Bi*x*Nd1*−x*VO4 as the Bi concentration increases.

The band gap energy of the monoclinic BiVO4 obtained by us (~2.38 eV) is in a good agreement with values reported in the literature ( ~2.4 eV [15–17]). From Fig. 9 it can be seen that the band gap of BiVO4 varies insignificantly with the nominal Nd concentration, which is consistent with the previous finding that Nd does not enter the crystal structure of BiVO4.

The UV-vis spectra of NdVO4, Bi*x*Nd1*−x*VO4 and Bi0.49Nd0.51VO4/BiVO4 composites show the presence of two different peaks centred at around 585 nm and 754 nm. These peaks (at the almost the same positions) have already been reported in the literature [51,53] and assigned to the electronic transitions of Nd3+ ion from 4I9/2 to 4G5/2 and from 4I9/2 to 4F7/2. This assignment is consistent with the fact that we have observed them for all the samples except for BiVO4.

3.2.2. Photoluminescence properties

Photoluminescence spectra of the monoclinic BiVO4 have been reported in the literature [15,22,29,38,54–56]. Most of the reported spectra show a broad peak in the range of 490-600 nm but with different intensity and peak position. These differences have been attributed to different synthesis method, particle size, and conditions of measurement (temperature, excitation wavelength etc). For example, BiVO4 prepared by the ultrasonic method [56] showed a broad band from 490 until 570 nm, with three maxima. The PL intensity of this sample was higher than the one of BiVO4 obtained by the solid-state method. The sample prepared in an aqueous medium [29] showed a peak centred at about 600 nm with a higher intensity at 77 K than at room temperature, while in [15] no PL signal was observed, even at 83 K. The monoclinic BiVO4, prepared by a liquid-solid reaction, gave a broad PL peak centred at about 715 nm [22]. Our spectrum of BiVO4 (Fig. 10) looks similar to the spectrum reported for the ~20 nm sized BiVO4 prepared via an ultrasound irradiation, measured at room temperature [55]. The broad peak in the emission spectrum of the BiVO4 powder was attributed to a radiative recombination of the holes, formed in the O 2p of the valence band, with the V3d0electrons in the conduction band.

From Fig. 10 we see that the PL spectra of BiVO4 and the nominal NdyBi1-yVO4 compositions have similar intensities (which is expected because Nd3+ does not enter the BiVO4 structure). In the case of the nominal NdyBi1-yVO4 compositions, an additional peak can be observed at ~605 nm which could originate from the Nd3+ ion electronic transition (viz. 4G7/2,9/2 →4I11/2, 13/2 [57]).

The PL spectra of Bi*x*Nd1*−x*VO4 powders are shown in Fig 11. Due to the electronic transitions inside the rare-earth ion (Nd3+), the NdVO4 spectrum shows more structures than the BiVO4 one. The nature of these transitions can be understood based on Judd-Ofelt theory [58]. In the tetragonal NdVO4, theNd3+ ions are located at the sites that lack the centre of symmetry (D2d symmetry) [39,59] which makes the electronic dipole transitions within the Nd3 4f shells possible. Calculation of the energy level diagrams for Nd3+ in NdVO4 can be found in [59]. The PL properties of NdVO4 upon UV excitation have so far been reported only for single-crystalline nanorods, measured with an excitation wavelength of 310 nm at room temperature [[53](file:///C:\Users\mvalant\AppData\Article_Mirela\References%20article%201\mirela13.pdf)]. The sharp emission bands in the wavelength range 350–500 nm, detected on the NdVO4 nanorods, are not present in the PL spectrum that we have recorded on the powders with around 1µm particle size, but we observed similar emissions in the interval of 500 - 650 nm as reported in [53,57,60,61]. Therefore, the emission peaks at ~503, 525, 556, 598, and 605-612 nm could be assigned to the 4G11/2 → 4I11/2 [57], 4G7/2 → 4I9/2 [60,61], 4G9/2 → 4I9/2[53,61], 4G5/2 → 4I9/2 and 4G7/2, 9/2 → 4I11/2, 13/2  transitions respectively [57].

PL spectrum lineshape of Bi*x*Nd1*−x*VO4 changes with respect to the spectrum of NdVO4, but the intensity and lineshape of PL spectra of BixNd1-xVO4 solid solutions do not change with the Bi concentration. There is a decrease of the emission intensity in the range of 425–600 nm with the appearance of sharp peaks at about 500 and 525 nm and a broad band with a maximum at about 545 nm. Moreover, in the range of 650–675 nm, a new triplet is clearly visible in the PL spectra of BixNd1-xVO4 solid solutions. The fact that the new triplet appeared only in BixNd1-xVO4 (x > 0) samples and not in the BiVO4 or NdVO4 spectra, shows that these new emissions are caused by the small modifications of the Nd3+ local structure in NdVO4 with the Bi3+doping (see section 3.1.2).

**4. Conclusions**

The phase relations and optoelectronic properties in the BiVO4-NdVO4 system have been reported. We have found that Bi substitutes Nd according to formula Nd1-xBixVO4 up to x = 0.49(1). The EXAFS study of Bi in the Bi0.2Nd0.8VO4 sample showed that the first oxygen atoms around Bi3+ are at a smaller distance as it could be expected from their ionic radii, which is a consequence of the hybridization of Bi6s2 and O 2p orbitals. By the Bi-doping, we succeeded to shift the absorption of NdVO4 towards the visible range of the solar spectrum and, so, to enhance its optical absorption. The decrease of the band gap has been attributed to the Bi 6s2 - O 2p hybridization at the top of the NdVO4 valence band. This is also in agreement with the observed reduction in the unit cell volume with the increase in concentration of the larger Bi3+ ion (increasing x) and the appearance of new emission lines in the PL spectra. On the other side of the BiVO4-NdVO4 system, Nd does not substitute either Bi or V in the BiVO4 structure.

**Acknowledgements**

The XAS experiments were performed at beamline C of HASYLAB at DESY, Hamburg (project I-20110082 EC). The work has been supported by the Slovenian Research Agency research programme P1-0112 and P2-0337, Centre of Excellence Low-Carbon Technologies (CO NOT) Slovenia, and by DESY and the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement CALIPSO n° 312284.".We would like to thank Roman Chernikov and Edmund Welter of HASYLAB, for support and expert advice on beamline operation.

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**Figure captions**

**Fig. 1.** X-ray diffraction patterns of Bi-doped NdVO4 samples with the nominal stoichiometry Bi*x*Nd1-*x*VO4. The filled circles denote the tetragonal NdVO4 phase (space group *I*41/*amd*), while the filled triangles represent the monoclinic BiVO4 phase.

**Fig. 2.** Unit cell variation of Bi*x*Nd1*-x*VO4 samples as a function of Bi concentration (x).

**Fig. 3.** X-ray diffraction patterns of Nd-doped BiVO4 samples with the nominal stoichiometry Nd*y*Bi1*−y*VO4. The tetragonal NdVO4-based phase is represented with the crosses, while the monoclinic BiVO4 phase is represented with the filled circles.

**Fig. 4.** Magnitude of Fourier transforms of the k2-weighted Bi L3-edge EXAFS of Bi0.2Nd0.8VO4, Nd L3-edge of NdVO4 and V K-edge in BiVO4 calculated in the k range of 4–11 Å-1.

**Fig. 5.** (A) The k2-weighted Bi and Nd L3-edge EXAFS spectra (dots) and best fit EXAFS models (solid line). (B) Fourier transforms magnitude of k2-weighted Bi L3-edge EXAFS in Bi0.2Nd0.8VO4 and of Nd L3-edge EXAFS in NdVO4 (solid lines), compared to their best fit EXAFS models (red dashed line) calculated in the R range = 1–4 Å (spectra are shifted for clarity).

**Fig. 6.** Fourier transform magnitude of the k2-weighted Nd L3-edge EXAFS measured on the sample with the Nd0.05Bi0.95VO4 nominal composition, compared to k2-weighted Bi L3-edge and V K-edge FT EXAFS spectra, measured on BiVO4 calculated in the k range of 3.5–10.5 Å-1.

**Fig. 7** (A)The k2-weighted Nd L3-edge EXAFS spectrum, measured on the sample with the Nd0.05Bi0.95VO4 nominal composition (dots), and its best fit EXAFS model (solid line). (B) Fourier transforms magnitude of the k2-weighted Nd L3-edge EXAFS spectrum (solid line), measured on the sample with the Nd0.05Bi0.95VO4 nominal composition, compared to the best fit EXAFS model (dashed line) calculated in the R range = 1.35–5.1 Å

**Fig. 8.** UV-Vis diffuse reflectance spectra of Bi*x*Nd1*-x*VO4 with x = 0, 0.1, 0.2, 0.3, and 0.4. The Kubelka-Munk function is plotted versus the excitation energy. The band gap (Eg) of NdVO4 decreased by Bi-doping. The insert shows the band gap determination of NdVO4.

**Fig. 9.** UV-Vis diffuse reflectance spectra of nominal NdyBi1-yVO4 compositions. The Kubelka-Munk function is plotted versus the excitation energy. The Eg of BiVO4 varies insignificantly with Nd concentration. The insert shows the band gap determination of BiVO4.

**Fig. 10.** Room temperature PL spectra of BiVO4 and nominal NdyBi1-yVO4 compositions.

**Fig. 11.** Room temperature PL spectra of Bi*x*Nd1*−x*VO4 powders.

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