LANTHANIDE DOPED BISMUTH TUNGSTATES: AN INVESTIGATION FOR LED AND PHOTOCATALYSIS APPLICATIONS

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ABSTRACT

In this work, we studied optical, photocatalytic and photoelectrochemical properties of a series of lanthanide-doped double layered Aurivillius type bismuth oxides. The visible-light harvesting photocatalysts doped with Eu, Pr, Nd, Tm, Ho and Ce ions were synthesized by solid-state synthesis method. Doping amount was varied between 0.2-to-10 percent. X-ray diffraction (XRD) analysis revealed that lanthanide atoms were incorporated into the Bi₂W₂O₉ lattice successfully up to 5%. Higher dopant ratios resulted in formation of secondary phases. Particles crystallized in micro-platelet morphology. Furthermore, luminescence of Pr³⁺ and Eu³⁺ ion doped catalysts are evaluated and the study showed that red emission intensity of Pr³⁺ doped powder is 29 times higher than that of Eu³⁺ doped ceramics. Lanthanide doped powders absorb in the visible regions. Especially, doping double layered bismuth oxide with Ce significantly narrowed down the band gap from ~3.3 eV to ~2.1 eV. Photoelectrochemical behaviour of the powders was also investigated and rare-earth dependent enhanced photocurrent production is demonstrated. Best photoelectrochemical response is achieved with Tm³⁺ ion doped sample.

Keywords: Perovskite oxide, Lanthanides, Luminescence, Photoelectrochemistry

1. INTRODUCTION

Photocatalysis is an attractive and promising future technology for renewable and sustainable energy challenge which includes clean energy production (H₂ production from water splitting), decrease in the CO₂ emission levels (by CO₂ reduction) and elimination of hazardous organic pollutants under solar light or other illuminating light sources. While UV absorbing TiO₂-based semiconductors are the most popular choice for photocatalysis, considerable amount of semiconductors have been tested to utilize visible portion of sun light and to increase efficiency [1]. Perovskite-related layered materials that consist of two-dimensional perovskite sheets separated with cations or cationic units are among these photocatalysts. Aurivillius phase layered perovskite Bi₃WO₈ has attracted considerable attention due to its good performance in photocatalytic water splitting and dye decomposition measurements [2],[3],[12],[4]–[11]. Although, the second member of the Bi₂W₆O₁₉³⁻ has been reported to display photocatalytic activity over ten times higher than Bi₂WO₆ for H₂ evolution and O₂ evolution under UV radiation [13], there are few reports on Bi₂W₂O₉ as a photocatalyst [13]–[15]. Furthermore, the band gap energy values (E₉) of Bi₂W₂O₉ is located between 2.87 - 2.96 eV [15], hence considerable portion of solar energy cannot be utilized. Photocatalysts with wider spectral response are required for exploiting higher amount of solar energy and layered materials allow development of visible-light-active perovskites through incorporation of dopant atoms at the interlayer space or in the lattice [1]. It is well

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known that trivalent rare earth ions with a high density of energy levels in the IR–UV range exhibit abundant absorption bands in the visible and even the infrared region. Hence, rare earth ions have been used to enhance the photocatalytic activities of metal oxides in the visible region [16],[17]. Rare earth ions have the potential to expand the visible light-response of metal oxides and decrease the recombination rate of the electron–hole through accelerated interfacial charge. Furthermore, the effect of lanthanide ion doping on the photocatalytic activity of Bi$_2$WO$_6$ has been studied [10],[18]–[20]. Er$^{3+}$-doped Bi$_2$WO$_6$ [21] and BiErWO$_6$ [10] showed good photocatalytic performance in degradation of Rhodamine B (RhB) under simulated solar light. Eu$^{3+}$-doped Bi$_2$WO$_6$ has been also shown to greatly improve photocatalytic activity [19],[22]. Rare earth-doped inorganic phosphors have also attracted attention due to their remarkable luminescent properties and applications in lighting, lasers, displays, drug carriers, photovoltaics, photocatalysis, and telecommunications [23]. Bismuth containing compounds are shown to be efficient host materials for phosphors since Bi$^{3+}$ ions can be replaced by rare earth ions, which can absorb outer energy, efficiently transferring from Bi$^{3+}$ to rare-earth ions [24]. To date, Bi$_2$WO$_6$ has been utilized as the host material for red-emitting phosphors by doping with Eu$^{3+}$ [12] or upconversion material [21]. However, luminescence of rare-earth doped Bi$_2$WO$_6$ is rarely studied. Yu Li et al. prepared a series of single crystal LnBiW$_3$O$_9$ compounds (Ln: Ce, Er, Sm, Eu) and studied luminescence properties of EuBiW$_3$O$_9$ [25]. The yellow-red emitting EuBiW$_3$O$_9$ has the potential to be utilized as red-emitting phosphor in light-emitting diode designs. Hence, detailed analysis of the optical properties of rare-earth doped Bi$_2$WO$_6$ compounds remains to be investigated.

In this work, we studied optical and photoelectrochemical properties of Lanthanide-doped Bi$_2$W$_3$O$_9$ (Ln: Eu, Ce, Pr, Ho, Tm and Nd) powders. The effect of dopant identity and concentration on optical and photoelectrochemical properties of the of rare-earth doped Bi$_2$W$_3$O$_9$ powders is discussed.

2. METHODS

2.1 Synthesis of the Photocatalysts

Double perovskite Bi$_2$W$_3$O$_9$ and lanthanide-doped Bi$_2$W$_3$O$_9$ (Ln_BWO) nano-powders were synthesized by the traditional solid-state reaction between Bi$_2$O$_3$, WO$_3$ and/or Ln$_2$O$_3$ (Ln = Eu, Pr, Ho, Tm and Nd) or CeO$_2$ provided by Alfa Aesar (99.9 %). A stoichiometric mixture prepared considering also charge neutrality was placed in a porcelain crucible and calcined at 800 °C for 48 h in 2-steps with intermittent grinding.

2.2 Characterization

Structural characterization was carried out by powder X-ray diffraction (XRD) using Bruker/D8 Advance Diffractometer with Cu Kα radiation. The surface morphologies of the films were examined with ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM). UV-diffuse reflectance spectra (DRS) of the oxides were measured using a Shimadzu UV-vis-NIR 3600 spectrophotometer equipped with an integration sphere. The luminescence of the powders was measured by Horiba Jobin Yvon–Fluoromax 3. Photoluminescence spectra were recorded between 370-800 nm.

2.3 Photoelectrochemical Characterization

Photoelectrochemical analyses were performed with Bio-Logic VSP model potentiostat/galvanostat system. The current–voltage (I–V) characteristics of the prepared films were measured under amplitude modulated-light illumination with the 3 electrode cell system with a Pt counter electrode and Ag/AgCl(satd) reference electrode. Cyclic voltammograms (CV) were measured under a potential sweep rate of 20 mV/s. 0.5 M Na$_2$SO$_4$ solution was used as a supporting electrolyte solution. N$_2$ saturation was made in the electrolytes before the electrochemical measurements. The working electrodes were prepared by electrophoretic deposition (EPD). Prior to the deposition, Fluorine tin oxide...
(FTO) electrodes (Teknoma Ltd. Izmir, Turkey) were washed with acetone, ethanol and DI water, subsequently in an ultrasonic bath. Two FTO electrodes with 1 cm² exposed areas were dipped into the suspension. The distance between the electrodes was 1 cm. EPD was carried out under 100 V for 10 min. 0.02 g of photocatalysts were dispersed in isopropyl alcohol (IPA) containing 5× 10⁻⁴ M aqueous Mg(NO₃)₂. EPD was carried out immediately after the suspensions were mixed in an ultrasonic bath for 30 min. and magnetically stirred for 10 min. Keithley 2400 Model source meter was used for deposition experiments. Following the deposition, the film was rinsed with ethanol and dried naturally.

3. RESULTS AND DISCUSSION

In this work, we studied photocatalytic and photoelectrochemical properties of lanthanide-doped Bi₂W₂O₉ powders. The effect of dopant identity and concentration on optical and photoelectrochemical properties of the powders is discussed. The doping amount ranges from 2 to 10 mol % of Bi.

3.1 Structure

The Bi₂W₂O₉ is the double layered member of the Aurivillius family of layered oxides which consists of alternating layers of (Bi₂O₂)²⁺ and double perovskite-like (W₂O₇)²⁻ layers. When Ln³⁺ ions are incorporated into the crystal lattice, the Bi³⁺ ion of (Bi₂O₂)²⁺ layers are expected be substituted [4].

Structure and phase of the as-prepared photocatalysts were characterized by XRD measurements. XRD patterns of the as-prepared Bi₂W₂O₉ and LnBi₂W₂O₉ (5 %) powders match well with the reported orthorhombic structure (space group: Pna21, JCPDS 04-011-0862) accompanied by minute impurities of Bi₂WO₆ in line with literature [26] (Figure 1). No reflections that belong to secondary phases such as Ln₂O₃ or lanthanide-related forms could be detected in these XRD diagrams. Preserved orthorhombic structure and absence of Ln₂O₃ related impurities imply that lanthanide atoms were incorporated into the Bi₂W₂O₉ lattice. Ionic radii of lanthanide ions -Eu³⁺ (94.7 pm), Pr³⁺ (99 pm), Nd³⁺ (98.3 pm), Tm³⁺ (88 pm), Ho³⁺ (90.1 pm) and Ce⁴⁺ (101 pm)- are smaller than that of Bi³⁺ (103 pm). Hence, substitution of Bi³⁺ ion with Ln³⁺ ions would result in reduced lattice spacing which could be detected by an increase in the observed Bragg reflections. Closer examination of diffraction patterns shows that the shift in the peak positions of LnBi₂W₂O₉ compared with parent Bi₂W₂O₉ is not significant. This may be due to low amount of doping. M. Tortosa et al. showed that doping levels lower than 9% may not induce a change in the lattice parameters [27].
Figure 2. Eu-doped Bi$_2$W$_2$O$_9$ compounds with different doping levels.

Figure 2 displays the enlarged patterns for selected 2θ ranges of the Eu-doped Bi$_2$W$_2$O$_9$ compounds with different doping levels. No reflections that belong to secondary phases such as Ln$_2$O$_3$ or related phases could be detected in the XRD diagrams up to 5% loadings. However, signs of phase separation and formation of phases such as Bi$_{12.67}$W$_{0.33}$O$_{20}$ (JCPDS 04-002-5754) is observed at and above 8% dopant levels. Similarly, Pr$^{3+}$ can be incorporated to the Bi$_2$W$_2$O$_9$ structure up to 5% (Figure 3).

Figure 3. Pr-doped Bi$_2$W$_2$O$_9$ compounds with different doping levels.

Figure 4 depicts a typical FE-SEM image of Bi$_2$W$_2$O$_9$ powders. Microstructures are composed of well-sintered, quadrangular micro-platelets. Size of the micro-platelets vary between 1-10 µm.
3.2. Optical Properties

Transformed DRS spectra of Bi$_2$W$_2$O$_9$ 2% and 10% doped samples are shown in Figure 5. Bi$_2$W$_2$O$_9$ has a steep absorption edge around 420 nm due to the band-edge transition (Figure 5b). All of the other samples shows this steep host absorption but it is red-shifted slightly to ~ 435, 444 and 450 nm for Nd_ Bi$_2$W$_2$O$_9$, Eu_ Bi$_2$W$_2$O$_9$ and Pr_ Bi$_2$W$_2$O$_9$. Ce_ Bi$_2$W$_2$O$_9$ exhibited the most profound red shift to around 650 nm absorbing a considerable portion of visible light which accounts for the brown colour of the powder. The significant red shift suggests narrower band gap for Ce_ Bi$_2$WO$_9$ which is attributed to charge transfer between the valance band of the host and 4f levels of the Ce ion [28]. Y. Li et al, reported EuBiW$_2$O$_9$, ErBiW$_2$O$_9$, SmBiW$_2$O$_9$ and CeBiW$_2$O$_9$ to be indirect band gap materials based on DFT calculations [25]. Hence, the optical band gap energy of the powders were calculated by Tauc plot [29], assuming indirect allowed transition. [$F(R)$hv]$^{1/2}$ was plotted against the photon energy, where F(R) is Kubelka–Munk function and hv is incident photon energy. The band gap energies for pristine, Nd_ Bi$_2$W$_2$O$_9$, Eu_ Bi$_2$W$_2$O$_9$, Pr_ Bi$_2$W$_2$O$_9$. Ce_ Bi$_2$W$_2$O$_9$ products are 3.18, 3.19, 3.17, 3.16 and 2.11 eV, respectively suggesting especially Ce_ Bi$_2$W$_2$O$_9$ to be a promising visible-light photocatalyst.
In addition to the slight shift of the host absorption peak, some characteristic transitions of the lanthanide ions are observed for Pr$_2$Bi$_2$WO$_9$, Nd$_2$Bi$_2$WO$_9$, Tm$_2$Bi$_2$WO$_9$ and Ho$_2$Bi$_2$WO$_9$ as indicated by the sharp absorption peaks in the visible region (Figure 4). Peaks observed at 447, 472, 486 and 597 nm for Pr$_2$Bi$_2$WO$_9$ are ascribed to the transitions from ground state of Pr$^{3+}$, $^3$H$_4$, to $^3$P$_2$, $^1$I$_6$, $^3$P$_1$, $^3$P$_0$ and $^3$D$_2$, respectively [8]. Characteristic absorption bands of Nd$^{3+}$ ions originating from the ground state, $^4$I$_{9/2}$, to higher excited states, $^4$G$_{9/2}$, $^2$G$_{7/2}$, $^2$G$_{5/2}$ + $^2$F$_{7/2}$, $^4$F$_{7/2}$, $^4$F$_{5/2}$, at 526, 583, 745, 801 and 870 nm can also be seen in Figure 4d [30]. The bands present in the absorption spectrum of Tm$_2$Bi$_2$WO$_9$ centred at 685 and 789 nm can be indexed to the transitions from the ground level, $^3$H$_6$, to $^3$F$_3$ and $^3$H$_6$, respectively [31]. The spectrum of Ho$_2$Bi$_2$WO$_9$ exhibits absorption bands in the visible region centred at 453, 453, 540 and 645 nm, which correspond to the transitions from ground state, $^5$I$_8$, to upper levels; $^5$G$_6$, $^5$F$_4$ and $^5$F$_3$, respectively [7]. In addition, the intensity of absorption bands of the rare earth ions is found to increase with increasing rare earth content as exemplified with Tm and Ho doped powders (Figure 5). The transitions of 4f electrons of the rare earth ions are expected to favour the separation of the photogenerated charge carriers which decreases the electron-hole recombination rate, thereby enhancing the photocurrent production efficiency. Moreover, the slightly red-shifted absorption edge as discussed above is considered to improve the photocatalytic activity under visible light [4],[32],[33]. Photoluminescence spectra of dispersed Pr$_2$Bi$_2$WO$_9$ and Eu$_2$Bi$_2$WO$_9$ powders with varying dopant amounts were measured at room temperature (Figure 6). Emission profiles of Eu$_2$Bi$_2$WO$_9$ powders depend on the excitation energy (Figure 6b-c). Upon excitation at 350 nm, Eu$_2$Bi$_2$WO$_9$ powders exhibit a number of emission bands in the range of 550–700 nm which originate from $^5$D$_0$→$^7$F$_{J}$ (J=0,1,2,3) transitions of Eu$^{3+}$ ion. The peaks at ~580, 588-596, 614-625 and 652 nm are indexed to $^5$D$_0$→$^7$F$_2$, $^5$D$_0$→$^7$F$_1$ and $^5$D$_0$→$^7$F$_3$, respectively with maximum emission at ~ 614 nm. The relative intensity of 614 nm emission line increases at the expense of the others when the sample is exited at 254 nm. Information
regarding the local environment of Eu$^{3+}$ ion in the host can be deduced from relative intensities of these emission lines [23],[34],[35]. The $^5D_0 \rightarrow ^7F_0$ transition at around 580 nm (observed under illumination at 350 nm) indicates a very low point group symmetry around Eu$^{3+}$ ion in Bi$_2$W$_2$O$_9$ since it is forbidden both by electric and magnetic dipole [25],[36]. The electric dipole (ED) transition, $^5D_0 \rightarrow ^7F_2$, is forbidden for the free ion or in the presence of inversion symmetry [34]. Hence, the induced ED transition is hypersensitive to the crystal field environment and its emission intensity is strongly affected by the strength of local electric field. Even small deviations from inversion symmetry will result in dominant red emission [37]. On the other hand, $^5D_0 \rightarrow ^7F_1$ transition is magnetic dipole (MD) allowed and insensitive to the crystal environment. Therefore, the intensity ratio of ED ($^5D_0 \rightarrow ^7F_2$) to MD ($^5D_0 \rightarrow ^7F_1$) transition (red to orange emission) which is defined as the asymmetry ratio serves as a measure of the site symmetry of the Eu$^{3+}$ ions in the host crystals. This value is reported to be 0.67 for centrosymmetric Eu$^{3+}$ ion and higher values imply lower symmetry [38]. It is reported that the $^5D_0 \rightarrow ^7F_0$ transition is only observed with $C_n$, $C_{nv}$ and $C_3$ symmetry [36]. Furthermore, the integral intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transition is calculated to be 1.70 for 5% Eu$_{50}$Bi$_{20}$W$_{20}$O$_{90}$ and 1.75 for 2% Eu$_{50}$Bi$_{20}$W$_{20}$O$_{90}$ for excitation at 350 nm and 4.9 and 2.5 for excitation at 254 nm, respectively. Hence, this emission profile (Figure 6b) implies that the local symmetry around Eu$^{3+}$ ion in Bi$_2$W$_2$O$_9$ is without an inversion centre. This is in line with XRD studies which suggest substitution of rare earth atoms in the crystal structure since all atoms in Bi$_2$W$_2$O$_9$ are reported to occupy $C_1$ symmetry sites [39].

![Photoluminescence spectra](image)

**Figure 6.** Photoluminescence spectra of a) Pr$_{50}$Bi$_{20}$W$_{20}$O$_{90}$ and b) Eu$_{50}$Bi$_{20}$W$_{20}$O$_{90}$ powders dispersed in distilled water and exited at 350 nm, c) Eu$_{50}$Bi$_{20}$W$_{20}$O$_{90}$ powders dispersed in distilled water and exited at 254 nm, d) luminescence intensity difference between Pr$_{50}$Bi$_{20}$W$_{20}$O$_{90}$ and Eu$_{50}$Bi$_{20}$W$_{20}$O$_{90}$.

We also report luminescence properties of Bi$_2$W$_2$O$_9$ powders doped with Pr$^{3+}$ ions for the first time, to the best of our knowledge. In the emission spectra Pr$_{50}$Bi$_{20}$W$_{20}$O$_{90}$ powders under 350 nm excitation, the emission bands of $^1D_2 \rightarrow ^3H_4$ display sharp peaks at around 601, 608, 620 (a weak shoulder) and 629
nm with due to characteristic de-excitation of $^{1}\text{D}_2$ multiplets of Pr$^{3+}$ ion [40]. The strongest emission is at 608 nm with excitation with UV light, which implies effective energy transfer between the host and the lanthanide ion. Furthermore, emission intensity increases with dopant amount for both Eu$^{3+}$ and Pr$^{3+}$ doped samples. The red emission intensity of Pr$^{3+}$ doped powder is 29 times higher than that of Eu$^{3+}$ doped ceramics (integral area). Hence, Pr$_{2}$Bi$_2$W$_9$O$_{39}$ with its intense red emission is a better candidate than Eu$_2$Bi$_2$W$_9$O$_{39}$ for utilization as red phosphor in designing white light-emitting diodes with highly intense emissions (Figure 6c).

3.3. Photoelectrochemical Properties

The photoelectrochemical properties of the electrodes prepared by electrophoretic deposition is investigated through transient photocurrent studies and linear voltammetry. Figure 7a shows the linear voltammetry scans (25 mV/s) of Bi$_2$W$_9$O$_{39}$ and Ln(2%)$_2$Bi$_2$W$_9$O$_{39}$ under pulsed illumination. The onset potential of the photocurrent was observed to appear at around -0.2 V (except for Ho$_{2}$Bi$_2$W$_9$O$_{39}$), and the photocurrent increased steadily with applied positive potential. The net photocurrent density ($I_{\text{photocurrent}}$ - $I_{\text{dark current}}$) produced by pure Bi$_2$W$_9$O$_{39}$ is higher than that of Eu$_2$Bi$_2$W$_9$O$_{39}$ and Pr$_{2}$Bi$_2$W$_9$O$_{39}$ while Ce$_{2}$Bi$_2$W$_9$O$_{39}$, Nd$_{2}$Bi$_2$W$_9$O$_{39}$ and Tm$_{2}$Bi$_2$W$_9$O$_{39}$ show enhanced photoelectrochemical activity than their undoped counterpart. The lower photocurrent suggests increased electron-hole recombination for Eu$_{2}$Bi$_2$W$_9$O$_{39}$ and Pr$_{2}$Bi$_2$W$_9$O$_{39}$. As discussed in the previous section, Bi$_2$W$_9$O$_{39}$ is very effective in absorbing UV light and transferring energy to Eu$^{3+}$ and Pr$^{3+}$ ions which results in strong luminescence. The exited electrons might be back-donated to the defect/donor band and recombine with the holes in the valance band, thereby decreasing photoelectrochemical efficiency. Ce$_{2}$Bi$_2$W$_9$O$_{39}$, Nd$_{2}$Bi$_2$W$_9$O$_{39}$ and Tm$_{2}$Bi$_2$W$_9$O$_{39}$, on the other hand, are more effective in separation of photogenerated electron–hole pairs than pure Bi$_2$W$_9$O$_{39}$. As discussed above, rather than inducing structural changes or forming impurity phases, lanthanide ions are incorporated into the Bi$_2$W$_9$O$_{39}$ lattice when the doping amount is 2%. The incorporation of lanthanide ions could form shallow energy level(s) between the conductance and valance band, thereby decrea
4. CONCLUSIONS

A series of lanthanide-doped double layered Aurivillius type bismuth oxides were prepared by solid-state synthesis. XRD diagrams revealed that introduction of lanthanide ions did not induce structural changes or result in impurity phases up to 5 % loadings. The local symmetry around Eu$^{3+}$ ion in Bi$_2$W$_2$O$_9$ together with XRD studies suggested that substitution of rare earth atoms in the crystal structure in the Bi$^{3+}$ sites. Pr$_2$Bi$_2$W$_2$O$_9$ and Eu$_2$Bi$_2$W$_2$O$_9$ powders displayed very strong red emission although luminesce intensity of Pr$_2$Bi$_2$W$_2$O$_9$ is much higher as compared to that of Eu$_2$Bi$_2$W$_2$O$_9$. Among the prepared photocatalysts, Tm(2%)$_2$Bi$_2$W$_2$O$_9$ exhibited highest photoactivity with 1.34 µA/cm$^2$ net photocurrent density at 0.5 V under 75 mW/cm$^2$ light, suggesting enhanced charge carrier separation with introduction of Tm into the structure.

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