Role of Gd in Enhancing the Charge Carrier Mobility of Spray–Deposited BiVO₄ Photoanodes

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The emergence of BiVO₄ as one of the most promising photoanodes for solar water splitting is largely driven by the success in dopant introduction and optimization to improve its photoelectrochemical performance. To this end, although less commonly used, several trivalent ions (e.g., In³⁺, Gd³⁺) that substitute Bi⁵⁺ have also been demonstrated to be effective dopants, which can increase the photocurrent of BiVO₄ photoanodes. However, the main factor behind such improvement is still unclear as various explanations were proposed in the literature. Herein, Gd³⁺ is introduced to substitute Bi⁵⁺ in spray-deposited BiVO₄ films, which enables up to a ~2-fold photocurrent increase. Further analysis suggests that Gd-doping enhances the carrier separation in BiVO₄ and does not affect the catalytic and optical properties. Indeed, time-resolved microwave conductivity measurements reveal that the carrier mobility of BiVO₄ is increased by 50% with the introduction of Gd, while the carrier lifetime is unaffected. This mobility increase is rationalized to be a result of a higher degree of monoclinic lattice distortion in Gd-doped BiVO₄, as evident from the X-ray diffraction and Raman spectroscopy data. Overall, these findings provide important insights into the nature and the underlying role of Gd in improving the performance of BiVO₄.

1. Introduction

Converting and storing solar energy as chemical energy through photoelectrochemical (PEC) water splitting is a promising approach to mitigate the global energy and environmental problems. The process utilizes semiconductor photoelectrodes to absorb sunlight and generate photoexcited electrons and holes, which drive the water oxidation or reduction reactions on their surfaces to form oxygen and hydrogen, respectively.[1-2] Metal oxides have been widely used as photoelectrode materials because of their general stability, multitude bandgap energies, relative abundance, and low synthesis cost.[3] Among the various metal oxides, bismuth vanadate (BiVO₄), particularly the monoclinic scheelite structure, has emerged as one of the most promising n-type oxide photoabsorbers for PEC water splitting.[4-6] Monoclinic BiVO₄ possesses a 2.4 eV bandgap, which allows visible light absorption, and favorable conduction and valence band positions for the water splitting reaction.[4-6] Nevertheless, the performance of unmodified BiVO₄ is limited by slow water oxidation kinetics[7] and poor carrier transport (i.e., mobility, lifetime) that limits the charge separation efficiency.[8,9] The latter is typically addressed by doping to tune the electrical properties of BiVO₄.[10] In particular, extrinsic doping, which is defined as the substitution or addition of a foreign element at the crystal lattice point of the host element,[11] has been widely applied to enhance the PEC performance of BiVO₄. For example, substituting V⁵⁺ with Mo⁶⁺,[12-14] W⁶⁺,[8,9,15,16] or both Mo⁶⁺ and W⁶⁺ simultaneously (i.e., codoping)[17-19] results in donor-doped BiVO₄ with increased carrier concentration. This enhances the electrical conductivity and, thus, the electron transport properties. Further enhancement of carrier separation has been reported by distributing the W⁶⁺ and Mo⁶⁺ composition throughout BiVO₄ (i.e., gradient doping).[20-22]
The substitution of Bi³⁺ in BiVO₄ with trivalent ions has also been reported. Interestingly, in contrast to the Mo or W doping described earlier, the isovalent nature of the dopants, in this case, is not expected to directly modify the carrier concentration of BiVO₄. Other roles have therefore been proposed. For example, the incorporation of In³⁺ in BiVO₄ was reported to inhibit surface charge recombination due to surface state passivation. Govindaraju et al. evaluated several lanthanide ions (La, Ce, Sm, and Yb) as dopants in BiVO₄ and reported multiple roles. Doping with La and Ce was found to decrease the PEC performance due to an increase of the effective mass of carriers (as shown from density functional theory, DFT) and/or an introduction of a midgap state that acts as recombination center. Meanwhile, Sm and Yb doping, despite the main 3+ oxidation state, indirectly increased the carrier concentration in BiVO₄ because of the coexistence of oxygen vacancies that introduced shallow donor states and enhanced the PEC performance. Gd has also been reported as an effective dopant in BiVO₄ photocatalyst powders, and higher photocatalytic activity for the degradation of methylene blue and rhodamine B was reported. It was suggested that the half-filled 4f electronic configuration of Gd⁴⁺ ions on the surface of BiVO₄ is beneficial for trapping charges and enhancing charge transfer for the catalytic reactions. An optimal Gd-doping concentration also simultaneously enhances the activity, selectivity, and stability of BiVO₄ for the water oxidation to H₂O₂ production. Newhouse et al. showed that Gd doping modified the monoclinic distortion in the lattice of BiVO₄, which was expected to decrease the hole effective mass as shown by their DFT results. Further improvement was demonstrated by combining Gd doping with an additional transition metal (W or Mo) as electron donor and H₂ annealing to improve the carrier lifetime. Overall, various assignments have been proposed, which demonstrates that the main role of trivalent dopants in BiVO₄, especially Gd, is still not clear. To unravel this, further investigation on the influence of trivalent ion doping on the photoelectrochemical properties (e.g., carrier transport and catalytic activity) of BiVO₄ is still needed.

In this study, we fabricated Gd-doped and (Gd,W)-co-doped BiVO₄ thin film photoanodes using spray pyrolysis, which demonstrate up to twice as high photocurrents as compared to that of pristine BiVO₄. This photocurrent enhancement is found to be a result of a higher charge separation efficiency, not catalytic efficiency. In contrast to W doping, Gd doping enhances the carrier mobility while maintaining the relatively long carrier lifetime in BiVO₄ as measured by time-resolved microwave conductivity (TRMO). To the best of our knowledge, this is the first direct experimental study that correlates Gd doping in BiVO₄ to the modulation of its carrier transport properties. Further effects of Gd doping on the optical, surface chemical composition, morphological, and structural properties of BiVO₄ will also be discussed.

2. Results and Discussion

2.1. Photoelectrochemical and Optoelectronic Properties of Gd–Doped BiVO₄

As slow surface reaction kinetics (i.e., slow hole transfer across the semiconductor/electrolyte interface) have been shown to limit the photocurrent of BiVO₄, sodium sulfite (Na₂SO₃) was added into the electrolyte in this study as hole scavenger to eliminate any surface catalytic limitations. Deposition of various cocatalysts (e.g., NiFeOOH and CoP₃) has been demonstrated to overcome this limitation in a hole-scavenger-free electrolyte, but this is not the focus of our work. The AM 1.5 photocurrent–voltage curves for BiVO₄ and 1% Gd–BiVO₄ films in 2 M KP, with and without 0.5 M Na₂SO₃ are shown in Figure 1. In both electrolytes, 1% Gd doping results in a significantly higher photocurrent and a cathodic shift of the onset potential of BiVO₄; the effect is more pronounced in the presence of hole scavengers. The Gd concentration was also varied up to 3% (Biₓ₋ₓₐₓ(Gdₓ,y,VO₄) x = 0, 0.005, 0.01, 0.02, and 0.03). The crystal structure of all these samples was found to be monoclinic scheelite BiVO₄, which will be shown and discussed in a later section of the manuscript. The AM 1.5 photocurrents at 1.23 V_RHE are plotted as a function of the Gd concentration, as shown in Figure 2 and Figure S1a, Supporting Information. All Gd-doped BiVO₄ films show higher photocurrents at 1.23 V_RHE than the undoped film, and 1% is found to be the optimum Gd concentration. The photocurrent of BiVO₄ and 1% Gd–BiVO₄ at 1.23 V_RHE is ≈1.8 and 3.4 mA cm⁻², respectively. This approximately twofold photocurrent improvement underlines the effectiveness of Gd doping in BiVO₄. We also note that the photocurrent of the 1% Gd–BiVO₄ film is of the same order as those reported for spray-pyrolyzed gradient-doped W–BiVO₄ films, which is among the highest for nonnanostructured BiVO₄.

We then combined Gd doping with W doping (i.e., codoping) because W has been widely used as a donor dopant to improve the electrical conductivity of BiVO₄. The AM 1.5 photocurrents of 1% W-doped BiVO₄ films with varying concentrations of Gd are shown in Figure S1b,c, Supporting Information (the synthesis of W-doped BiVO₄ and (Gd,W)-codoped BiVO₄ films is described in Supporting Note S1, Supporting Information). Gd doping is also effective in improving the photocurrent of W-doped BiVO₄, and the same optimum concentration of 1% Gd was found. Surprisingly, the photocurrents of the (Gd,W)-codoped BiVO₄ films are lower than those of Gd-doped films. This observation is in contrast to the case of (Gd, Mo)-codoped BiVO₄ films, as reported by Newhouse et al. The

![Figure 1](https://www.solar-rrl.com)
After the blank quartz substrate, the inset shows photographs of the (left to right) blank quartz substrate, BiVO₄, and 1% Gd–BiVO₄ on quartz. Tauc plots for direct and indirect bandgap analysis of BiVO₄ and 1% Gd–BiVO₄ films.
The fact that no significant catalytic or absorption changes could be observed upon Gd doping suggests that the improved photoelectrochemical properties are related to the enhancement of the charge separation efficiency. A possible factor that may increase the charge separation efficiency is an increase of conductivity due to higher carrier concentration. This is, however, unlikely to be the case as Gd is an isovalent dopant and we will discuss later that the process of introducing Gd into our BiVO₄ should not be compensated for with any electronic or ionic defects. We therefore evaluate the charge transport properties of both undoped and 1% Gd–BiVO₄ by performing TRMC measurements. Briefly, both films are excited with a nanosecond laser pulse ( photon energy $h\nu$ > bandgap), resulting in the formation of free electrons and holes, which are then detected as a change in the microwave power reflected from the samples. This change corresponds to the change of photoconductance ($\Delta G$), which is then monitored as a function of time (i.e., transient). The relative comparison of the peak transient can be used to evaluate the charge carrier mobility, and the charge carrier lifetime can be obtained from the transient decay.$^{13,37}$

Figure 4a shows the transient photoconduction responses, normalized to the absorption ($F_\lambda$) and photon flux ($I_0$), for the undoped and 1% Gd–BiVO₄ films. The measurements were performed under backside 350 nm laser pulse illumination (i.e., $h\nu \approx 3.5 \text{ eV} > E_g$ of BiVO₄), and the $I_0$ was $4.3 \times 10^{13}$ pulse$^{-1}$ cm$^{-2}$. Upon Gd doping, the peak $\Delta G/(F_\lambda I_0)$ transient increases by a factor of 1.5, which indicates an improvement of the charge carrier mobility. In contrast, the transient decay does not seem to be affected. This can be seen clearly from Figure 4b, in which the transient photoconductance of each sample is normalized against the peak value (i.e., $\Delta G/\Delta G_{\text{max}}$). Both transients overlap with each other, which indicates that the charge carrier lifetime of BiVO₄ is unaffected by Gd doping. This also suggests that the charge transport mechanism is likely to be the same in both films. Similar effects to the transient peak and decay can also be observed for other excitation wavelengths (see Figure S3, Supporting Information). Overall, the higher mobility and constant lifetime with Gd doping result in an extended charge carrier diffusion length, which can explain the enhanced charge separation and observed photocurrent improvement.

2.2. Influence of Gd Incorporation on the Chemical, Morphological, and Structural Nature of Spray–Deposited BiVO₄

We now investigate the underlying chemical, morphological, and structural changes associated with the introduction of Gd into our BiVO₄, which may be responsible for the improvement of the carrier mobility. The presence of Gd in the Gd-doped BiVO₄ films is first confirmed by performing X-ray photoelectron spectroscopy (XPS). Bi 4f, V 2p, O 1s, and Gd 4d core-level spectra of undoped BiVO₄, 1% Gd–BiVO₄, and 3% Gd–BiVO₄ films are shown in Figure 4, Supporting Information. Although the Gd 4d spectra are rather noisy due to the low concentration, Gd can be detected in the Gd-doped films, and the introduction of Gd does not introduce any changes to the Bi 4f, V 2p, or O 1s spectra. This is not surprising, since the isovalent substitution of Bi with Gd (i.e., Gd$_{Bi}$) does not require any ionic or electronic compensations. Based on the XPS spectra, we found that the Gd atomic concentration of 1.3% and 2.9% was calculated for the 1% Gd–BiVO₄ and 3% Gd–BiVO₄ films, respectively.

The Gd incorporation was then evaluated for any influences in the morphology of the BiVO₄ films. Figure 5 shows the top-view scanning electron micrographs of undoped BiVO₄, 1% Gd–BiVO₄, and 3% Gd–BiVO₄ films. Similar interconnected irregular grain features can be observed from all films, and the grain size is slightly increased with increasing Gd doping concentrations: 183 ± 58 nm for undoped BiVO₄, 218 ± 57 nm for 1% Gd–BiVO₄, and 289 ± 96 nm for 3% Gd–BiVO₄. An increase in grain size would reduce the amount of grain boundary scattering, and this has been demonstrated to be the cause for an increase in charge carrier mobility and photocurrent.($^{18,39}$) However, the continuous increase of grain size with increasing Gd concentration does not agree with the presence of the photocurrent maximum for the 1% Gd concentration. This suggests that the cause behind the enhanced charge carrier mobility and photoelectrochemical performance in our films is unlikely to be related to the morphology change.

![Figure 4](https://www.solar-rrl.com/images/figure4.png)

**Figure 4.** a) Transient photoconductance, $\Delta G/(F_\lambda I_0)$, signals and b) normalized photoconductance, $\Delta G/\Delta G_{\text{max}}$, recorded for BiVO₄ (black) and 1% Gd–BiVO₄ (red) under backside 350 nm laser pulse illumination with a photon flux, $I_0$, of $4.3 \times 10^{13}$ pulse$^{-1}$ cm$^{-2}$. 

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Finally, the influence of Gd doping on the crystal structure of BiVO₄ films is investigated by performing X-ray diffraction and Raman spectroscopy measurements. Figure 6a shows the grazing incidence X-ray diffraction patterns for undoped BiVO₄, 1% Gd–BiVO₄, and 3% Gd–BiVO₄ films. Reference diffraction patterns of monoclinic and tetragonal scheelite BiVO₄ are also shown. The distinction between the tetragonal and monoclinic scheelite is that the local environments of V and Bi ions are more notably distorted in the monoclinic versus tetragonal structure. As a result, two different V–O bond lengths are present in monoclinic scheelite, whereas there is only one V–O bond length in tetragonal scheelite.[40] All our BiVO₄ films show diffraction peaks that match well with those of monoclinic scheelite BiVO₄ without any impurity phases. In contrast to other reports,[26,27] we do not observe a transition from monoclinic to tetragonal scheelite in our BiVO₄ films with Gd doping, which will be discussed later. Figure S6, Supporting Information, shows that the (121) peak position slightly shifts to a higher 2θ angle upon Gd doping. This shift is consistent with the notion of substituting Bi³⁺ ions (ionic radius = 1.17 Å) with Gd³⁺ ions (1.05 Å),[41] which has also been shown in a report of Gd-doped Bi₂O₃ powder.[42]

A closer look at the {110} and {240} X-ray diffraction peaks (Figure 6b,c) reveals that the monoclinic peak splits further apart with higher Gd concentration, suggesting increased distortion of the crystal lattice with Gd incorporation in our films. To confirm this observation, Raman spectroscopy was performed to shed light on the short-range order and the V–O bond lengths in our films. The Raman spectra are indicated in Figure 7 and the positions of the assigned Raman bands are given in Table S1, Supporting Information. All the Raman peaks agree with those described in previous reports on monoclinic scheelite BiVO₄.[28,29,43,44] Consistent with the XRD results, the structural change from monoclinic scheelite to tetragonal scheelite, which can be identified by the merging of peaks belonging to the symmetric bending mode δₛ(VO₄²⁻) and asymmetric bending mode δₘ₅(VO₄²⁻) into one,[28,29,44] is not observed with Gd incorporation into our films (see Figure 7b). Instead, as the discontinuity in the dashed lines shows, δₛ(VO₄²⁻) and δₘ₅(VO₄²⁻) slightly shift to higher wavenumber with Gd incorporation. The same shift to higher wavenumber is also observed for the symmetric and asymmetric V–O stretching mode νₛ(V–O) and νₘ₅(V–O); see Figure 7c). Based on the empirical relationship reported by Hardcastle et al.,[45,46] the V–O bond lengths can be calculated using the following equation

$$\nu = 21349 \exp(-1.9176R)$$  \hspace{1cm} (3)

where is the Raman stretching frequency in cm⁻¹ (symmetric and asymmetric) and R is the V–O bond length in angstrom.
Finally, we discuss the possible reason for the difference in observation between our Gd-doped BiVO₄ films and those reported in the literature.²⁶,²⁸,²⁹ Whereas reports in the literature suggest that Gd incorporation induces a transition from monoclinic to tetragonal, we instead show that this is not the case in our spray-deposited BiVO₄ films. One possible reason is that we maintain a relatively low Gd dopant concentration in our study. Another possible reason, which we believe is more likely, is related to the different synthesis procedures, specifically in the way that stoichiometry is maintained in the resulting Gd-doped BiVO₄. In studies reported in the literature, a Bi:V ratio of 1:1 was maintained in the Gd-doped films. This can be represented by a dissolution reaction of Gd₂O₃ into the lattice of BiVO₄, as shown in the Kröger–Vink notation.³⁰

\[
\text{Gd}_2\text{O}_3 \rightarrow 2\text{Gd}^{3+}_\text{Bi} + 2\text{V}^{4+}_\text{Bi} + 3\text{O}^{2-}_\text{O} + 5\text{V}^{3+}_\text{O} \quad (4)
\]

The introduction of Gd is compensated for by the formation of vanadium and oxygen vacancies (V⁴⁺_/V³⁺ and V³⁺_/O²⁻). These vacancies may affect the crystal structure as well as the photoelectrochemical performance of the resulting BiVO₄. An alternative defect chemical reaction can be written in the presence of excess oxygen during dissolution, but the formation of vanadium vacancies remains

\[
\text{Gd}_2\text{O}_3 + \frac{5}{2}\text{O}_2(g) + 10e^- \rightarrow 2\text{Gd}^{3+}_\text{Bi} + 2\text{V}^{4+}_\text{Bi} + 2\text{V}^{3+}_\text{O} + 8\text{O}^{2-}_\text{O} \quad (5)
\]

In our study, however, we did not maintain the Bi:V ratio to be 1:1. Instead, we kept the (Bi+Gd):V ratio as 1:1. This is typically written as a codoping process in the defect chemical equation; i.e., excess V was introduced along with the Gd-doping.

\[
\text{Gd}_2\text{O}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{Gd}^{3+}_\text{Bi} + 2\text{V}^{3+}_\text{O} + 8\text{O}^{2-}_\text{O} \quad (6)
\]

As shown previously, using this method, the introduction of Gd as dopant is not accompanied by the formation of any vacancies. We therefore speculate that the formation of these vacancies is the driving force for the transition from the monoclinic to tetragonal phase shown in the literature. Overall, this comparison underlines the importance of controlling the stoichiometry in the doping process of complex metal oxides.

3. Conclusion

In summary, we successfully introduced Gd as dopants in spray-pyrolyzed BiVO₄ films. Gd doping enhances the AM 1.5 photocurrent density, and 1 at% Gd is found to be the optimal concentration, resulting in a twofold improvement of the photocurrent density. Time-resolved microwave conductivity data suggest that the photocurrent improvement is caused by the increase of charge carrier mobility, which in turn results in better charge separation. Detailed structural analysis of the films via X-ray diffraction and Raman spectroscopy measurements reveal that Gd doping introduces further distortion of the monoclinic lattice by the reduction of the V–O bond lengths. This distortion has been correlated to the increase of photogenerated hole mobility,³⁴,³⁵ which is consistent with our TRMC results. Finally, by
comparing these findings with previous literature reports on Gd-doped BiVO₄, we propose alternative defect reactions associated with introducing Gd into monoclinic BiVO₄ and highlight the delicate nature of doping in ternary metal oxides.

4. Experimental Section

Spray Pyrolysis of BiVO₄ and Gd-Doped BiVO₄ Thin Films: BiVO₄ and Gd-doped BiVO₄ films were prepared by spray pyrolysis, which is a low-cost, facile, and scalable process for depositing BiVO₄ thin films.[51,52] The BiVO₄ precursor solution was prepared by dissolving 0.8 mmol of Bi(NO₃)₃·5H₂O (98%, Sigma–Aldrich) in acetic acid and dissolving 0.8 mmol VO(acac)₂ (99%, Alfa Aesar) in absolute ethanol. To prevent premature oxidation by trace amounts of water, triethyl orthoformate (TEOF, 98%, Fluka Analytical) was added to the Bi and V solution (TEOF reacts with water to form ethyl formate and ethanol).[51] The V solution was then added to the Bi solution, and the mixture was diluted with excess absolute ethanol to end up with a final precursor concentration of 4 mM. The ratio of acetic acid to ethanol in the final solution was 1:9. For the Gd-doped BiVO₄ (Biₓ·GdₓVO₄) solution, x = 0.005, 0.01, 0.02, and 0.03, Gd(NO₃)₃·6H₂O (99%, Sigma–Aldrich) was used as the Gd precursors. Varying amounts of Gd(NO₃)₃·6H₂O were added to the Bi precursor solution. The V solution was then added to the (Biₓ·Gdᵧ) solution, resulting in a mixture containing (Biₓ·Gdᵧ):V in a 1:1 ratio. TEC 7 FTO-coated glass or quartz was used as the substrate, which was cleaned by three successive 15 min ultrasonic cleaning treatments in acetone, absolute ethanol, and deionized water. The substrate temperature during spray was maintained at 450 °C. The spray deposition was carried out using an automated spray setup with a Quickmist air atomizing nozzle.[53] The spray rate of 1 mL per spray cycle consisted of 5 s of spray time and 55 s of delay time to allow solvent evaporation. The precursor solution (180 mL) was sprayed onto the heated substrate with a spray rate of 1 mL per spray cycle. For films deposited on FTO-coated glass substrates, a thin SnO₂ layer was spray deposited onto the FTO substrate prior to the BiVO₄ deposition using 5 mL of 0.1 M SnCl₂ solution in ethyl acetate, to prevent the recombination of electrons and holes at the FTO/BiVO₄ interface according to the previously reported procedure.[53] As a final step, all of the samples were annealed at 450 °C for 2 h with a heating rate of 5 °C min⁻¹ in air to further improve the crystallinity.

Characterization: UV–vis spectroscopy was performed using a Lambda 950 spectrophotometer (Perkin Elmer) equipped with an integrating sphere. TRMC measurements were performed using a home-built setup described in more detail previously.[18,37,54] In short, the BiVO₄ and Biₓ·Gdᵧ·VO₄ films deposited on quartz were placed in a microwave cavity during spray deposition. During the measurements, a change in the microwave power was performed using a LEO GEMINI 1530 instrument from ZEISS operated under backside illumination using a solar simulator (WACOM WXS–505–5 H, class AAA) with a scan rate of 25 mV s⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Keywords

BiVO₄, carrier mobility, Gd doping, photoelectrochemical water splitting, time-resolved microwave conductivity

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