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SOLVOTHERMAL AND HYDROTHERMAL SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF $BiVO_4$

Abstract. This study explores the synthesis of Bismuth vanadate ($BiVO_4$) using solvothermal and hydrothermal methods. The synthesized materials were characterized using X-ray diffraction and Raman spectroscopy. Energy Dispersive Spectroscopy confirmed the presence and uniform distribution of Bismuth, Vanadium, and Oxygen in both samples. Raman spectroscopy indicated higher local crystallinity in the hydrothermal method, while XRD showed higher overall crystallinity in the solvothermal method. These findings suggest that the hydrothermal method enhances local order, whereas the solvothermal method achieves better crystalline overall structure, that it is providing insights of optimizing $BiVO_4$ future synthesis investigations for renewable energy applications.

Key words: Bismuth vanadate, $BiVO_4$, Solvothermal synthesis, Hydrothermal synthesis, Crystallinity, Photocatalysis, Renewable energy.

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СОЛВОТЕРМАЛЬНЫЙ И ГИДРОТЕРМАЛЬНЫЙ СИНТЕЗ И СТРУКТУРНАЯ ХАРАКТЕРИСТИКА $BiVO_4$

Аннотация. В данном исследовании изучается синтез ванадата висмута ($BiVO_4$) с использованием сольвотермального и гидротермального методов. Синтезированные материалы были охарактеризованы методами рентгеновской дифракции и рамановской спектроскопии. Энергодисперсионная спектроскопия подтвердил наличие и равномерное распределение висмута, ванадия и кислорода в обоих образцах. Рамановская спектроскопия показала более высокую локальную кристалличность при гидротермальном методе, тогда как XRD показал более высокую общую кристалличность при сольвотермальном методе. Эти результаты свидетельствуют о том, что гидротермальный метод улучшает локальный порядок, в то время как с сольвотермальным методом достигается наилучшая кристалличность всей структуры, что дает представление об оптимизации будущих исследований синтеза $BiVO_4$ для применения в возобновляемых источниках энергии.

Ключевые слова: ванадат висмута, $BiVO_4$, сольвотермальный синтез, гидротермальный синтез, кристалличность, фотокатализ, возобновляемая энергия.

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Annotatsiya. Ushbu tadqiqotda vismut vanadat ($BiVO_4$) ni solvotermal va gidrotermal usullardan foydalanib sintez qilindi. Sintezlangan materiallar rentgen nurlari diffraktsiyasi va Raman spektroskopiyasi yordamida tavsiflangan. Energiya dispersiv spektroskopiyasi ikkala namuna tarkibida vismut, vanadiy va kislorodning mavjudligini va bir xilda taqsimlanishini tasdiqladi. Raman spektroskopiyasi gidrotermal usulda yuqori lokal kristallikni ko‘rsatdi, XRD esa solvotermal usulda umumiy kristallikning yuqoriligini ko‘rsatdi. Ushbu natijalar, gidrotermal usul lokal tartibni yaxshilashini, solvotermal usul esa yaxshiroq umumiy kristallik tuzilishini ta‘minlashini ko‘rsatdi. Bu esa $BiVO_4$ sintezini qayta tiklanadigan energiya manbalari uchun materiallarni optimallashtirish bo‘yicha tanlov imkonini beradi.

Kalit so‘zlar: Bismut vanadat, $BiVO_4$, Solvotermal sintez, Gidrotermal sintez, Kristallik, Fotokataliz, Qayta tiklanadigan energiya.

Introduction

Bismuth vanadate ($BiVO_4$) is a promising material for various applications, particularly in photocatalysis and photoelectrochemical water splitting, due to its suitable band gap and high stability [1-2]. Its potential to enhance solar energy conversion efficiency has garnered significant attention in recent years. Unique properties of $BiVO_4$ make it an attractive candidate for improving the performance of photoelectrochemical cells and photocatalytic systems [3]. The synthesis methods and the resulting material properties play a crucial role in optimizing its performance. Therefore, understanding and optimizing the synthesis of $BiVO_4$ is essential for advancing its practical applications in renewable energy technologies. $BiVO_4$ can be synthesized using various methods, including solid-state reactions, sol-gel processes, and precipitation methods [4]. Among these, solvothermal and hydrothermal methods are particularly effective in producing high-purity and well-crystallized materials [5-6]. These methods involve the use of solvents under controlled temperature and pressure conditions, leading to the formation of desired crystalline structures. Solvothermal synthesis typically uses organic solvents, while hydrothermal synthesis employs water as the solvent [7-8]. Both methods allow for precise control over the reaction environment, which is critical for tailoring the properties of the synthesized $BiVO_4$. This study aims to synthesize $BiVO_4$ using both solvothermal and hydrothermal methods for further characterization and testing for photocatalytic reaction.

Experimental section

Materials

Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), Vanadyl acetylacetonate ($C_{10}H_{14}VO_5$), acetic acid (AA) were purchased from Sigma-Aldrich. All reagents used in this work were of analytical grade and were used as received without any further purification. Pure Ethanol and distilled water were used for washing (cleaning) of synthesized $BiVO_4$.

Solvothermal synthesis

Dissolve 0.01 mol of $Bi(NO_3)_3 \cdot 5H_2O$ in 40 mL of acetic acid to prepare Solution A, stirring for 2 h until completely dissolved. Similarly, dissolve 0.005 mol of $C_{10}H_{14}VO_5$ in 30 mL of acetic acid to prepare Solution B, stirring for 2 h until fully dissolved. Slowly add Solution B to Solution A using a drop-casting technique while continuously stirring at 500 rpm, and continue stirring for 2 h until a yellowish solution forms. Then, we kept this solution for 24 h in dark place at room temperature. Collect the precipitate by centrifuging at 2500 rpm for 10 minutes, then wash several times with ethanol and distilled water to remove any impurities. Finally, dry the product at 60°C for 12 hours. Schematic illustration of the synthesis process is given in Figure 1.

Hydrothermal synthesis

Similar process like solvothermal process was done. After getting yellowish solution we transferred it to a Teflon-lined autoclave, seal it, and heat at 160°C for 12 hours. After the reaction, allow the autoclave to cool to room temperature naturally. The same process was repeated for separate material from the solution as mentioned at solvothermal synthesis.

Both samples which synthesized by solvothermal and hydrothermal were annealed at 500°C for 1 h in the muffle furnace to get better crystallinity of $BiVO_4$.

Structural characterization

The crystalline structure and phase purity of the synthesized $BiVO_4$ samples were analyzed using X-ray diffraction (XRD) by AL-27MINI equipment. The diffraction patterns were recorded in the 2θ range of 10° to 80°. Raman spectra of the $BiVO_4$ samples were recorded using a Probe Raman Spectrometer with a laser excitation wavelength of 785 nm. The spectra were collected in the range of 100 cm^{-1} to 1000 cm^{-1} to identify the characteristic vibrational modes of $BiVO_4$.

Results and discussion

The Energy Dispersive Spectroscopy (EDS) results for the $BiVO_4$ synthesized via the solvothermal method are shown in Figure 1 (above). The EDS spectrum displays peaks for Bismuth (Bi), Vanadium (V), and Oxygen (O), confirming their presence. The elemental mapping images indicate a uniform

distribution of Bi, V, and O throughout the sample. The Bi-M, V-K, and O-K lines are clearly visible, demonstrating successful incorporation of these elements into the $BiVO_4$ structure. Figure 1 (bottom) presents the EDS results for the $BiVO_4$ the $BiVO_4$ structure. Figure 1 (bottom) presents the EDS results for the $BiVO_4$

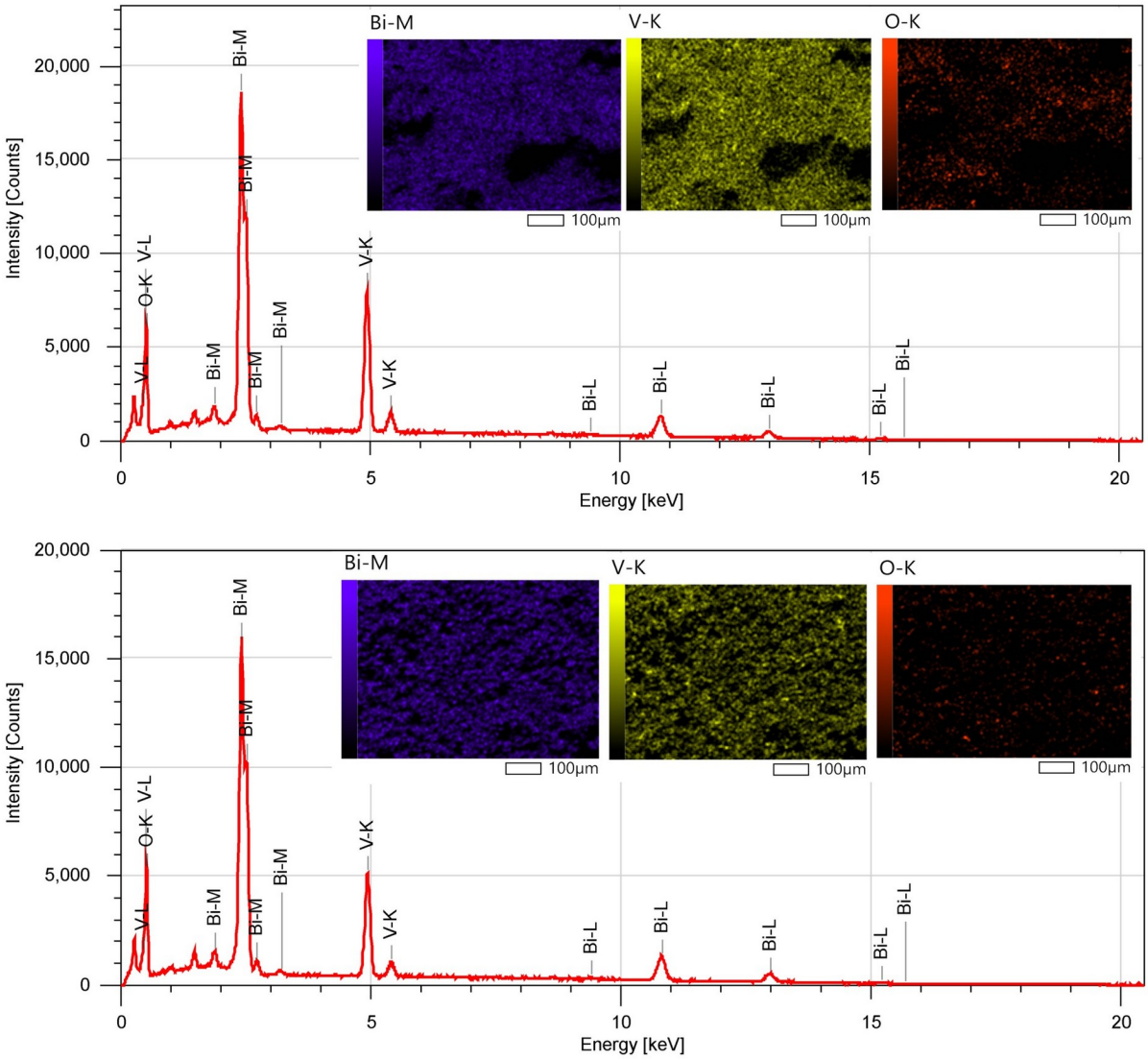

Figure 1. EDS results of $BiVO_4$ synthesized using solvothermal (above) and hydrothermal (bottom) methods.

synthesized using the hydrothermal method. The EDS spectrum also shows peaks for Bi, V, and O, verifying their presence. Elemental mapping images illustrate a uniform distribution of Bi, V, and O, indicating homogeneous composition. The intensity of the Bi-M, V-K, and O-K peaks is consistent with the solvothermal method, indicating similar elemental composition between the two methods.

Bi, V and O atomic percentages of $BiVO_4$ sample synthesized by solvothermal methods were 18.73, 21.81 and 59.45, respectively, where hydrothermal showed 19.07, 16.70 and 64.23. Both samples showed almost stoichiometric ratio between elements.

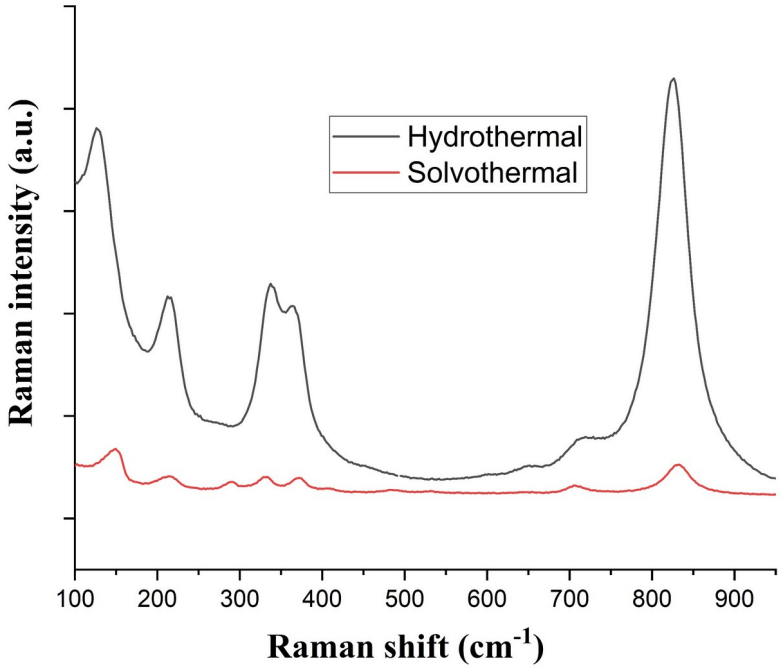

Figure 2. Raman spectra of $BiVO_4$ synthesized using solvothermal (red) and hydrothermal (black) methods.

The Raman spectra of $BiVO_4$ synthesized via solvothermal and hydrothermal methods are presented in the Figure 2. The spectra provide insights into the vibrational modes and crystallinity of the synthesized materials. The Raman spectrum for $BiVO_4$ synthesized using the solvothermal method (red line) shows characteristic peaks at around 200 cm^{-1}, 325 cm^{-1}, 367 cm^{-1}, and 827 cm^{-1} [9]. These peaks correspond to the vibrational modes of $BiVO_4$. The lower intensity of these peaks suggests a lower degree of crystallinity or smaller crystallite size compared to the hydrothermal method. The Raman spectrum for $BiVO_4$ synthesized using the hydrothermal method (black line) also exhibits characteristic peaks at around 200 cm^{-1}, 325 cm^{-1}, 367 cm^{-1}, and 827 cm^{-1}. However, the intensity of these peaks is significantly higher, indicating a higher

degree of crystallinity and larger crystallite size compared to the solvothermal method.

The XRD patterns for $BiVO_4$ synthesized via solvothermal and hydrothermal methods are shown in the Figure 3. The patterns provide information about the crystalline phases and structural properties of the materials. The XRD pattern for BiVO4 synthesized using the solvothermal method (red line) shows prominent peaks corresponding to the (110), (011), (121), (040), (200), and (002) planes [10]. The sharp and intense peaks indicate good crystallinity of the synthesized $BiVO_4$. The XRD pattern for $BiVO_4$ synthesized using the hydrothermal method (black line) shows similar peaks corresponding to the same planes. However, the peaks are broader and less intense, suggesting lower crystallinity compared to the solvothermal method.

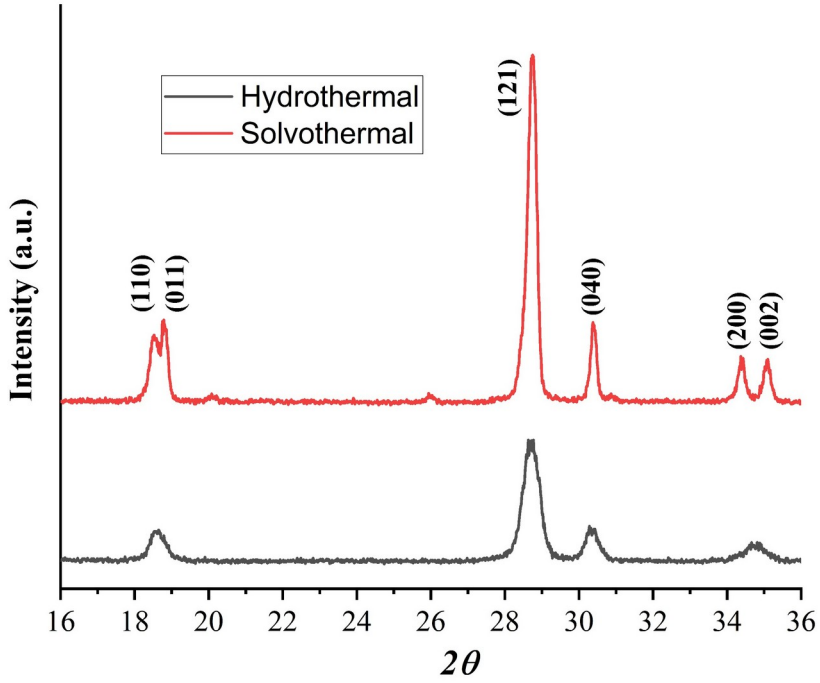

Figure 3. XRD of $BiVO_4$ synthesized using solvothermal (red) and hydrothermal (black) methods.

The Raman spectroscopy results indicate that the $BiVO_4$ synthesized via the hydrothermal method has higher crystallinity compared to the solvothermal method. This is evidenced by the more intense and sharper Raman peaks for the hydrothermal sample. Conversely, the XRD results show that the $BiVO_4$

synthesized via the solvothermal method has higher crystallinity, as indicated by the sharper and more intense XRD peaks.

The opposite results observed in Raman and XRD analyses may be due to differences in the sensitivity of these techniques to different aspects of the material's structure. Raman spectroscopy is highly sensitive to local vibrational modes and can provide detailed information about short-range order and molecular vibrations. Therefore, it might detect higher local crystallinity in the hydrothermal sample.

On the other hand, XRD is more sensitive to long-range order and overall crystallinity in the material. The broader XRD peaks in the hydrothermal sample suggest that, while local order may be higher (as detected by Raman), the overall crystallinity is lower, possibly due to smaller crystallite sizes or increased micro-strain in the hydrothermal sample. In summary, the hydrothermal method may produce BiVO4 with higher local order but lower overall crystallinity, while the solvothermal method yields $BiVO_4$ with higher overall crystallinity, as detected by XRD.

Conclusion

In this study, $BiVO_4$ was successfully synthesized using both solvothermal and hydrothermal methods. Characterization through XRD and Raman spectroscopy confirmed the formation of the desired phase. EDS analysis demonstrated the presence of key elements with uniform distribution. Raman spectroscopy indicated higher local crystallinity in the hydrothermally synthesized samples, while XRD analysis revealed that the solvothermal method produced $BiVO_4$ with higher overall crystallinity. These results suggest that the hydrothermal method enhances local order and vibrational properties, whereas the solvothermal method is more effective for achieving a well-defined overall crystalline structure. Future research will focus on optimizing these synthesis methods to further enhance the material properties and explore their implications for photocatalytic efficiency and other functional applications.

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