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Bismuth Vanadate ($BiVO_4$) Powder Prepared by the Sol-gel Method

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Abstract

Bismuth vanadate ($BiVO_4$) powder was prepared by the sol-gel method. Bismuth nitrate and ammonium vanadate were used as the starting precursors with mole ratio of 1:1 in ethanol at 70°C for 1 hour. The obtained sol was changed to the yellow gel after addition of deionized water and acetic acid. The yellow gel was dried at 100°C for 48 h and calcined at 400-600°C for 2 hours. The phase of $BiVO_4$ powder was studied by X-ray diffraction (XRD). The morphology of $BiVO_4$ powder was investigated by scanning electron microscopy (SEM). The element composition of $BiVO_4$ powder was indicated by energy dispersive X-ray spectrometry (EDS).

Key words: Bismuth vanadate, $BiVO_4$, Sol-gel method

Introduction

Bismuth vanadate ($BiVO_4$) is one of the photocatalysts, which has been recently recognized as a high potential application for degradation of organic pollutants in wastewater.(1-4) $BiVO_4$ is also a commercially available high performance pigment in the coatings and plastics industry. It is classified as non-toxic and could replace toxic pigments such as lead, cadmium and chromate based paints.(5) There are three phases reported for $BiVO_4$, monoclinic scheelite, tetragonal scheelite and tetragonal zircon. It was reported that tetragonal $BiVO_4$ with a 2.9 eV band gap mainly possessing a UV absorption band, while monoclinic $BiVO_4$ with a 2.4 eV band gap has a characteristic visible light absorption band besides the UV band. Photophysical and photocatalytic properties of $BiVO_4$ are strongly influence by the way of preparation and its crystal structure. Only the monoclinic scheelite $BiVO_4$ shows good visible- light activity. The photocatalytic activity of the monoclinic $BiVO_4$ prepared by the aqueous process at room temperature was much higher than that of monoclinic $BiVO_4$ prepared by a conventional solid-state reaction even in the same crystal structure.(6-9) The phase transition between monoclinic scheelite structure and tetragonal scheelite structure of $BiVO_4$ reversible occurs at about 255°C (ferroelastic to paraelastic transition), whereas the irreversible transition from tetragonal zircon type structure to monoclinic $BiVO_4$ occurs after heat treatment at 400-500°C and cooling to room temperature.(7) Monoclinic is obtained by the aqueous process from layered vanadates at room temperature,(8) whereas monoclinic $BiVO_4$ is prepared by solid state reaction starting from the metallic oxides at temperature above 600°C. Tetragonal with a zircon type is prepared by a precipitation method at room temperature.(9-10) Thus, the obtained crystal form depends on the preparation method. Several methods have been reported for the synthesis of $BiVO_4$ such as solid-state method,(9) sonochemical method,(11) organic decomposition method,(12) sol-gel method,(13) precipitation method,(14) hydrothermal method.(15) However, agglomeration and secondary growth often occur when we dry the wet particles separated from the reaction solution.

The sol-gel processing has low temperature chemical method used for preparation of organic oxide materials which has been widely used in the fields of materials science, ceramic engineering, in the preparation of photocatalysts. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid. The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to continuous chain-like polymer networks. Such a process may be obtained single and

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multi-component oxides as crystalline or amorphous form. It has also given bulk materials but suitable for thin film coating production. There are many advantages in sol-gel process during conventional method in synthesis oxide materials which have the possibility of changing the film features extensively through altering the composition of the solution as well as in a relatively low process cost.(16-17)

This paper reports the $BiVO_4$ powder prepared by the sol-gel method because of its advantage over other methods; lower processing temperatures; short annealing times, high purity of materials and good control of the size and shape of the particles. The structural phase of $BiVO_4$ powder was studied by X-ray diffraction (XRD). The morphology of $BiVO_4$ powder was investigated by scanning electron microscopy (SEM) and the element composition of $BiVO_4$ powder was indicated by energy dispersive X-ray spectrometry (EDS).

Materials and Experimental Procedures

The experimental procedure for preparing bismuth vanadate ($BiVO_4$) powder by the sol-gel method is schematically shown in Figure 1. Bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$) and ammonium vanadate (NH_4VO_3) were used as the starting precursors with molar ratio of 1:1. Solution A: 0.03M ($Bi(NO_3)_3{\cdot}5H_2O$) dissolved in 50 ml of 4M nitric acid (HNO_3) and solution B: 0.03M (NH_4VO_3) dissolved in 50 ml of 4M ammonium hydroxide (NH_4OH) were mixed together with stirring for 30 min. After solution A and B were mixed, yellow solution was obtained. The solution was then added with 100 ml ethanol (C_2H_5OH) and heated at 70°C with stirring for 1 hour. The yellow sol solution was obtained. Sol was changed to the yellow gel after addition 50 ml of deionized water and 5 ml of 1M acetic acid (CH_3COOH). Finally, the yellow gel was dried in oven (637G, Fisher Scientific, USA) at 100°C for 48 h and calcined in furnance (301, Carbolite, UK) at 400-600°C for 2 hours.

The crystalline phase of $BiVO_4$ powder was identified by X-ray diffractometer (X'Pert Pro MPD, Panalytical, Netherlands) with CuK_α radiation. The detection range was 10-60° with a step of 0.10° (°2θ/s/s), and the diffraction pattern was compared with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No. 14-0688. The morphology and particle size of $BiVO_4$ powder were investigated by scanning electron microscope (JSM5410-LV, JEOL, Japan) with the tungsten filament K type, accelerate voltage of 15.0 kV and working distance of 15 mm. The $BiVO_4$ powder was milled, sieved and dispersed with absolute ethanol (C_2H_5OH) medium in an ultrasonic bath (Cole Parmer, UK) for 15 min. Gold coating was performed by finer coater (JFC1200, JEOL, Japan) for 150 sec. The chemical composition was analyzed by an energy dispersive X-ray spectrometer (ISIS 300, Oxford, UK).

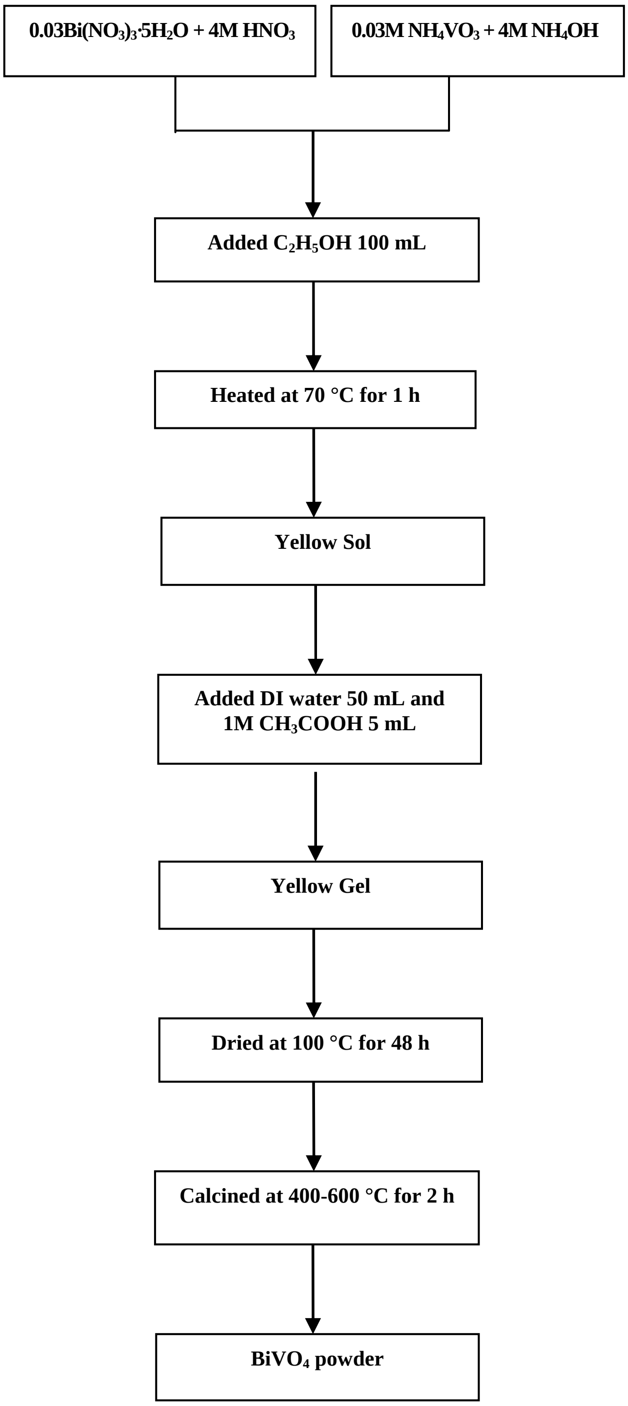


Figure 1. Schematic diagram of $BiVO_4$ powder prepared by the sol-gel method.

Results and Discussion

The phase structure of $BiVO_4$ powder was studied by X-ray diffraction (XRD). The XRD pattern reveals that all $BiVO_4$ crystallites with a monoclinic single phase structure after calcinations at 400-600°C for 2 hours (shown in Figure 2) No peaks of any other phases or impurities were found from secondary phase has been detected. The XRD intensity of $BiVO_4$ powder after calcination at 600°C for 2 hours is the strongest. The ratio intensity of the 011 and 121 diffraction peak increase with the rise in temperature. As the calcinations temperature increased, the line width decreased and intensity of diffraction line increased. It is well known that lattice parameters are temperature dependent, which was in good agreement with the previously reported.(18-20) Also, all peaks can be indexed to monoclinic $BiVO_4$ (JCPD file no.14-0688).(21)

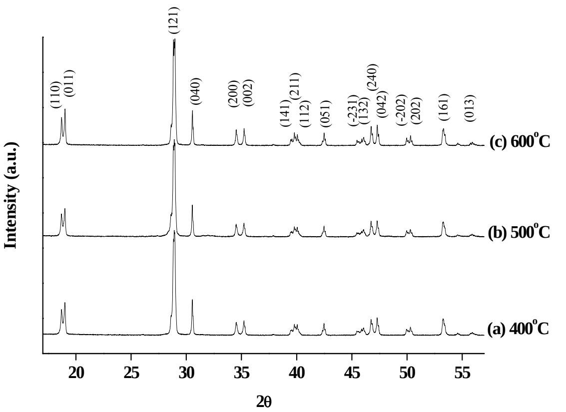
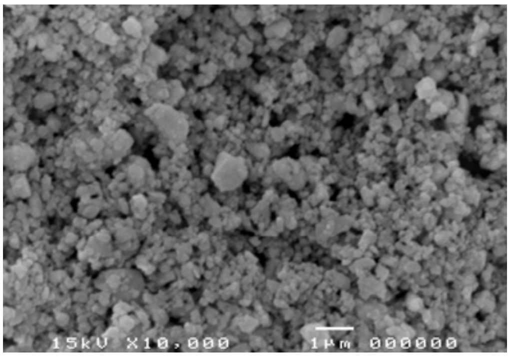
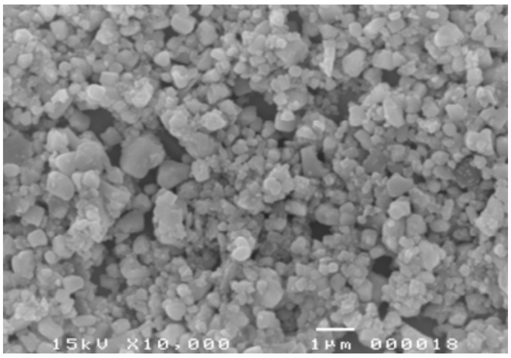


Figure 2. XRD pattern of $BiVO_4$ powder prepared by the sol-gel method after calcinations at (a) 400°C (b) 500°C and (c) 600°C for 2 hours.

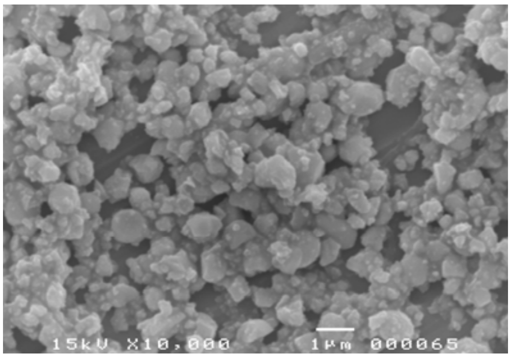
SEM micrographs of $BiVO_4$ powder after calcination at 400-600°C for 2 hours are shown in Figure 3. The particle of $BiVO_4$ powder prepared by the sol gel method was irregular in shape. The tendency of agglomeration is more at higher temperature than lower temperature. It was observed that the particle size increased with increasing temperature. $BiVO_4$ powder after calcination at 400°C for 2 hours has the average particles size of 0.3-0.5 µm (Figure 3 (a)). With the increasing temperature at 500°C and 600°C, the particle was larger with average particle size of 0.5-0.7 µm (Figure 3 (b)) and 0.7-1.0 µm (Figure 3(c)), respectively. The average particle size from this study was smaller than the previously reported.(20, 22)



a) 400°C



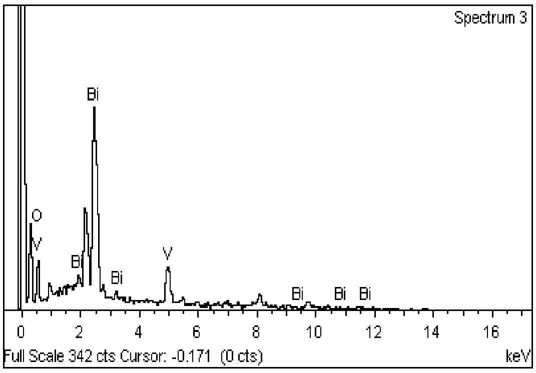
b) 500°C



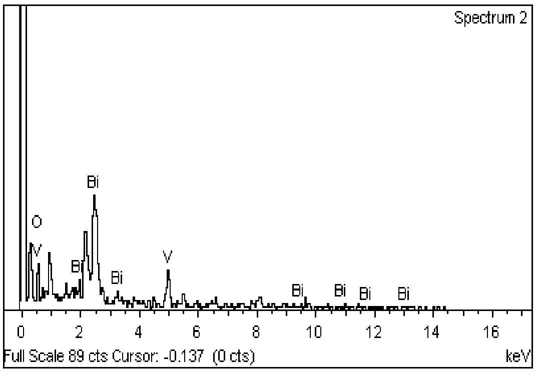
c) 600°C

Figure 3. SEM of $BiVO_4$ powder prepared by the sol-gel method after calcination at (a) 400°C, (b) 500°C and (c) 600°C for 2 hours.

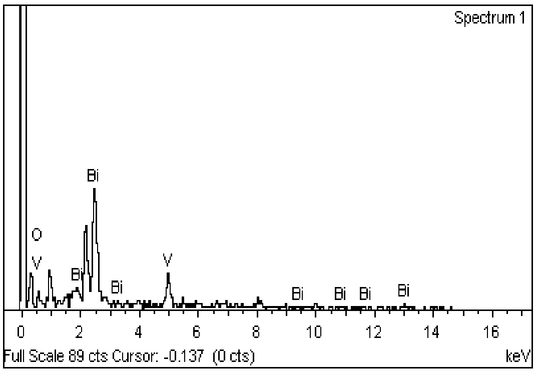
The elemental composition of $BiVO_4$ powder prepared by the sol-gel method after calcination at 400-600°C for 2 hours is shown in Figure 4. It indicates that the single phase of $BiVO_4$ powder consists of bismuth (Bi), vanadium (V) and oxygen (O) only. The characteristic X-ray radiation of each element had different energy values; bismuth L_α=10.84, L_β=13.0, M_α=2.42 and M_β=2.53 keV vanadium K_α =4.95, K_β=5.42, L_α=0.52 and L_β=0.51 keV and oxygen K_α=0.52 keV, respectively.(23)



a) 400°C



b) 500°C



c) 600°C

Figure 4. EDS of $BiVO_4$ powder prepared by the sol-gel method after calcination at (a) 400°C, (b) 500°C and (c) 600°C for 2 hours.

Conclusions

Bismuth vanadate ($BiVO_4$) powder was prepared by the sol-gel method with bismuth nitrate and ammonium vanadate as precursors. Single phase monoclinic structure of $BiVO_4$ powder was obtained after calcination at 400-600°C for 2 hours. It was found that the temperature significantly influenced the morphology. The average particle size at higher temperature was larger than lower temperature. The powder was agglomerated, irregular in shape with the average particle size in the range of 0.3-1.0 µm with increasing temperature.

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References

1. Zhou, B., Qu, J., Zhao, X. and Liu, H. (2011). Fabrication and photoelectrocatalytic properties of nanocrystalline monoclinic $BiVO_4$ thin-film electrode. *J. Environ. Sci. China*. **23(1)** : 151-159.

2. Wenzong, Y., Wenzhong, W., Lin, Z., Songmei, S. and Ling, Z. (2010). CTAB-assisted synthesis of monoclinic $BiVO_4$ photocatalyst and its highly efficient degradation of organic dye under visible-light irradiation. *J. Hazard. Mater*. **173**: 194-199.

3. Yingana, G., Xia, Y., Fengyan, M., Kexin, L., Lei, X., Xing, Y. and Yihang, G. (2010). Additive-free controllable fabrication of bismuth vanadates and their photocatalytic activity toward dye degradation. *Appl. Surf. Sci*. **256**: 2215-2222.

4. Silva, M. R., Dall'Antonia, L. H., Scalvi, L. V. A., Santos, D. I., Ruggiero, L. O. and Urbano, A. (2012). Deposition and characterization of $BiVO_4$ thin films and evaluation as photoanodes for methylene blue degradation. *J. Solid State Electrochem*. **16**: 3267-3274.

5. Smith, H. M. (2002). *High performance pigment*. Weinheim : Wiley-VCH-GbbH : 435

6. Ge, L. (2008). Novel visible-light-driven Pt/$BiVO_4$ photocatalyst for efficient degradation of methyl orange. *J. Mol. Catal. A: Chem*. **282** : 62-66.

7. Bhattacharya, A. K., Mallick, K. K. and Hartridage, A. (1997). Phase transition in $BiVO_4$. *Mater. Lett.* **30** : 7-13.

8. Kudo, A., Omori, K. and Kato, H. (1999). A novel aqueous process for preparation of crystal form-controlled and highly crystalline $BiVO_4$ powder from layered vanadates at room temperature and its photocatalytic and photophysical properties. *J. Am. Chem. Soc.* **121(49)** : 11459-11467.

9. Gotić, M., Musić, S., Ivanda, M., Šoufek, M. and Popović, S. (2005). Synthesis and characterization of bismuth(III) vanadate. *J. Mol. Struct.* **744-747** : 535-540.

10. Tokunaga, S., Kato, H. and Kudo, A. (2001). Selective preparation of monoclinic and tetragonal $BiVO_4$ with scheelite structure and their photocatalytic properties. *Chem. Mater.* **13**: 4624-4628.

11. Zhou, L., Wang, W., Liu, S., Zhang, L., Xu, H. and Zhu, W. (2006). A sonochemical route to visible-light-driven high-activity $BiVO_4$ photocatalys. *J. Mol. Catal. A: Chem.* **252** : 120-124.

12. Hai-qing, J., Hiromitsu, E., Hirotaka, N., Masayuki, N. and Koichi, K. (2008). Fabrication and photoactivities of spherical-shaped $BiVO_4$ photocatalysts through solution combustion synthesis method. *J. Eur. Ceram. Soc.* **28** : 2955-2962.

13. Min, W., Qiong, L. and Haiyan, L. (2011). Preparation, characterization and photocatalytic property of $BiVO_4$ photocatalyst by sol-gel method. *Appl. Mech. Mater.* **99-100**: 1307-1311.

14. Wood, P. and Glasser, F. P. (2004). Preparation and properties of pigmentary grade $BiVO_4$ precipitated from aqueous solution. *Ceram. Int.* **30** : 875-882.

15. Liu, J. B., Wang, H., Wang, S. and Yan, H. (2003). Hydrothermal preparation of $BiVO_4$ powders. *Mat. Sci. Eng. B.* **104** : 36-39.

16. Brinker, C. J. and Scherer, G. W. (1990). *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*. California : San Diego.

17. Alain, C. P. (1998). *Introduction to Sol-Gel Processing*, Norwell, Massachusetts : Kluwer.

18. Pookmanee, P., Paosorn, S. and Phanichphant, S. (2010). Chemical Synthesis and characterization of bismuth vanadate powder. *Adv. Mater. Res.* **93-94** : 153-156.

19. Ghosh, P. K., Das, S. and Chattopadhyay, K. K. (2005). Temperature dependent structural and optical properties of nanocrystalline CdO thin films deposited by sol–gel process. *J. Nanopart. Res.* **7** : 219-225.

20. Pookmanee, P., Pingmuang, K., Kangwansupamomkon, W. and Phanichphant, S. (2010). Methylene blue degradation over photocatalyst bismuth vanadate powder synthesized by the hydrothermal method. *Adv. Mater. Res.* **93-94** : 177-180.

21. Joint Committee on Powder Diffraction Standards (JCPDS). *Powder Diffraction File, Card* No. 14-0688. Pennsylvania : Swarthmore.

22. Zhang, X., Ai, Z., Jai, F., Zhang, L., Fan, X. and Zou, Z. (2007). Selective synthesis and visible-light photocatalytic activities of $BiVO_4$ with different crystalline phases. *Mater. Chem. Phys.* **103** : 162-167.

23. Woldseth, R. (1973). *X-ray Energy Spectrometry. Kevex* California : Corp.