

# Synthesis of nanometer sized $\text{Bi}_2\text{WO}_6$ s by a hydrothermal method and their conductivities

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**Abstract**—Nanometer-sized bismuth tungsten oxides,  $\text{Bi}_2\text{WO}_6$ s, were successfully synthesized by hydrothermal treatment at 200 °C for 24 hr, and their morphologies and crystallite sizes were influenced by adjusting the conditions to pH 4, 7, and 9. TEM images revealed that the particles were sheet-shaped and the crystallite sizes ranged from 7-120 nm. The samples absorbed in the visible range at about 380-400 nm. The lowest conductivity,  $1.0 \times 10^6$  ohm/square, was observed for  $\text{Bi}_2\text{WO}_6$  prepared at pH 4 with a 150 nm film thickness. As the annealing temperature for  $\text{Bi}_2\text{WO}_6$  prepared at pH 7 was increased, the conductivity decreased due of formation of larger particles by coagulation and sintering at high temperatures. Conductivity appears to improve with increasing film thickness up to 1,500 nm.

Key words: Nanometer-sized Bismuth Tungsten Oxide, Hydrothermal Treatment, pH, Conductivity

## INTRODUCTION

Recently, nanostructured tungsten materials, such as  $\text{Bi}_2\text{WO}_6$ ,  $\text{Bi}_2\text{MO}_6$ ,  $\text{Bi}_2\text{W}_{1-x}\text{Cu}_x\text{O}_{6-2x}$ , and  $\text{Sb}_2\text{WO}_6$ , have generated much interest because of their potential application in various fields, such as in photoluminescence, fiber-optics, scintillation materials, and photocatalysts [1-4], due to their unique combination of physical and chemical properties, such as electronic versatility, reactivity, and stability. Most recently, Cruz et al. [5] reported that  $\text{Bi}_2\text{WO}_6$ - $\text{Sb}_2\text{WO}_6$  could be used in electrochemical cells, and Fung et al. [6] reported that orthorhombic  $\text{Bi}_2\text{WO}_6$  sintered at high temperatures (800 and 1,000 °C) has conductivity. Furthermore, when the content of Cu and Mg in  $\text{Bi}_2\text{WO}_6$  increases, the conductivities are improved by the increased number of oxygen vacancies. Also, substitution of Mg rather than Cu for W is superior in reducing the proportion of orthorhombic  $\text{Bi}_2\text{WO}_6$  and increasing that of the tetragonal phase. [6] We investigated the influence of pH during hydrolysis on the morphology of  $\text{Bi}_2\text{WO}_6$ s prepared using a common hydrothermal method. Powdered samples were coated on PET film, their conductivities determined in terms of surface resistance (ohm/square), and the optimum conditions sought regarding the influence of annealing temperature and film thickness on conductivity.

## EXPERIMENTAL

### 1. Preparation of $\text{Bi}_2\text{WO}_6$ Nanometer Particles and $\text{Bi}_2\text{WO}_6$ /PET Films

$\text{Bi}_2\text{WO}_6$  nanometer particles were prepared by using a commercial hydrothermal method [7]. The  $\text{Bi}^{3+}$  ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 99.9%, Junsei Chemical, Japan) and  $\text{W}^{6+}$  ( $\text{WCl}_6$ , 99.9%, Junsei Chemical, Japan) ion precursors were mixed in the mole ratio of 1.0/2.0 in distilled water, the pH adjusted (using aqueous acetic acid and ammonia) to 4, 7, and 9, and stirred for 5 hr to achieve a homoge-

neous phase. The resulting solution was autoclaved (Model R-211, Reaction Engineering Inc., Korea), by heating to 200 °C at 5 °C/min and held there for 24 hr in a 5 atm nitrogen environment. During thermal treatment, bismuth and tungsten were hydrolyzed by OH groups from water and formed crystallites of  $\text{Bi}_2\text{WO}_6$  with an orthorhombic structure. The powders produced were then washed in water and dried at 100 °C for 24 hr.

To determine the conductivity (or resistance), the crystallized  $\text{Bi}_2\text{WO}_6$  particles were fixed upon PET (Polyethylene Terephthalate) films by using a binder prepared in-house and by a method described previously [8,9]. The resulting  $\text{Bi}_2\text{WO}_6$ /PET films were thin and transparent with a thickness of about 350 nm and visible light transmittance of 85%.

### 2. Characterization of Synthesized $\text{Bi}_2\text{WO}_6$ Nanometer Particles

The prepared  $\text{Bi}_2\text{WO}_6$ 's were examined by powder X-ray diffraction analysis (XRD, model PW 1830, Philips) with nickel-filtered  $\text{CuK}_\alpha$  radiation (40 kV, 100 mA). The sizes and shapes of the particles were determined by scanning electron microscopy (SEM, Model JEOL-JSM35CF, Tokyo, Japan) and high-resolution transmission electron microscopy (TEM, Model JEOL 2000EX, Japan) and Raman spectra acquired on an RFS 100/s FT-Raman spectrometer using a 102 mV 1,064 nm laser (Ld-YAG laser, Spectra-Physics Lasers, USA) focused on the sample under a microscope. The conductivity, judged by surface resistance, was estimated by a SIMCO Worksurface tester (Model ST-3, Japan) providing a 15 V potential difference and a current up to 1.5 mA between the parallel conductive probes. The UV-visible spectra of the powders were obtained with a Shimadzu MPS-2000 spectrometer (Kyoto, Japan) with a reflectance sphere.

## RESULTS AND DISCUSSION

### 1. Characterization of Synthesized $\text{Bi}_2\text{WO}_6$ Nanometer Particles

The XRD patterns (a), SEM, and TEM images (b) of the  $\text{Bi}_2\text{WO}_6$

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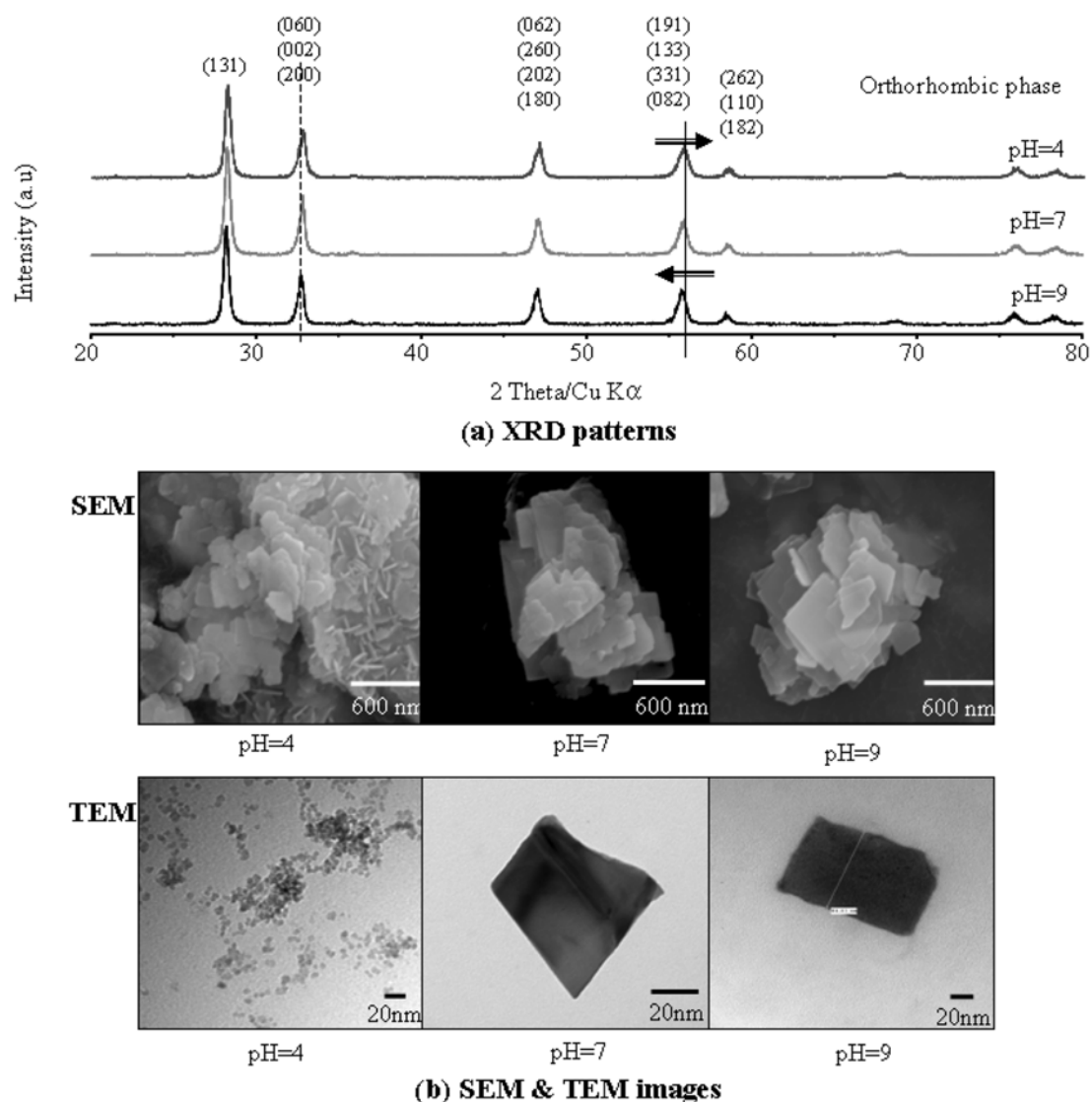


Fig. 1. The XRD pattern (a), SEM, and TEM images (b) of  $\text{Bi}_2\text{WO}_6$  prepared at different pH conditions.

particles at a ratio of Bi 1.0/W 2.0 prepared at the various pHs are shown in Fig. 1. The  $\text{Bi}_2\text{WO}_6$  particles exhibited an orthorhombic structure with peaks at 28.3, 32.7, 47.1, 55.7, and 58.5, which are assigned to the ( $d_{131}$ ), ( $d_{200,060}$ ), ( $d_{180,202,260}$ ), ( $d_{082,133,191}$ ), and ( $d_{182,110,262}$ ) planes, respectively [6,10]. The peak positions and intensities varied with the pH, shifting to the right in samples prepared in acidic solution. Notably, no other peaks typical of  $\text{Bi}_2\text{O}_3$  or  $\text{WO}_3$ , which would indicate their presence on the surface of the  $\text{Bi}_2\text{WO}_6$  framework, were seen in any of the XRD patterns. However, the line widths of the peaks were broad, indicating small crystalline domain sizes. Scherrer's equation,  $t = 0.9 \lambda / \beta \cos \theta$ , where  $\lambda$  is the wavelength of the incident X-rays,  $\beta$  is the full width at half maximum height in radians, and  $\theta$  is the diffraction angle, was used to calculate the crystalline domain sizes of 28.4, 37.4, and 42.5 nm for the  $\text{Bi}_2\text{WO}_6$  samples prepared at pH 4, 7, and 9, respectively. In addition, the  $\text{Bi}_2\text{WO}_6$  particle sizes increased with pH, as shown in Fig. 1(b). The average grain size from TEM micrographs ranged from 7.0 nm (pH 4) to 120 nm (pH 9), and the particles appeared very similar in SEM pictures. Generally, the SEM images appear differently from TEM im-

ages and the visible particles are agglomerates, not primary particles, such that discussion of particle sizes from SEM images must be approached with care. As TEM images show single particles, it was more reliable for the present purposes. The  $\text{Bi}_2\text{WO}_6$  particles presented sheet-like shapes and their size was largest when prepared in basic solution, owing to the dense forms induced by abrupt hydrolysis in basic solution.

Fig. 2(a) and (b) show the Raman and UV-visible spectra of the  $\text{Bi}_2\text{WO}_6$  particles. Zhu et al. [11,12] recorded the reference Raman spectra for the  $\text{Bi}_2\text{WO}_6$  orthorhombic structure: the peaks in the range of 600–1,000  $\text{cm}^{-1}$  were assigned to the stretching of W–O bonds, bands at 790 and 820  $\text{cm}^{-1}$  for  $\text{Bi}_2\text{WO}_6$  associated with anti-symmetric and symmetric  $A_g$  modes of the terminal O–W–O, respectively, and the bands at 310  $\text{cm}^{-1}$  assigned to the translation modes involving the simultaneous motions of  $\text{Bi}^{3+}$  and  $\text{WO}_4$ . We also observed three bands (at about 310, 710, and 800  $\text{cm}^{-1}$ ), but these bands were shifted to a lower wavenumber compared to those in the above study. A higher stretching mode wavenumber indicates a more distorted structure, whereas a lower such wavenumber indicates a

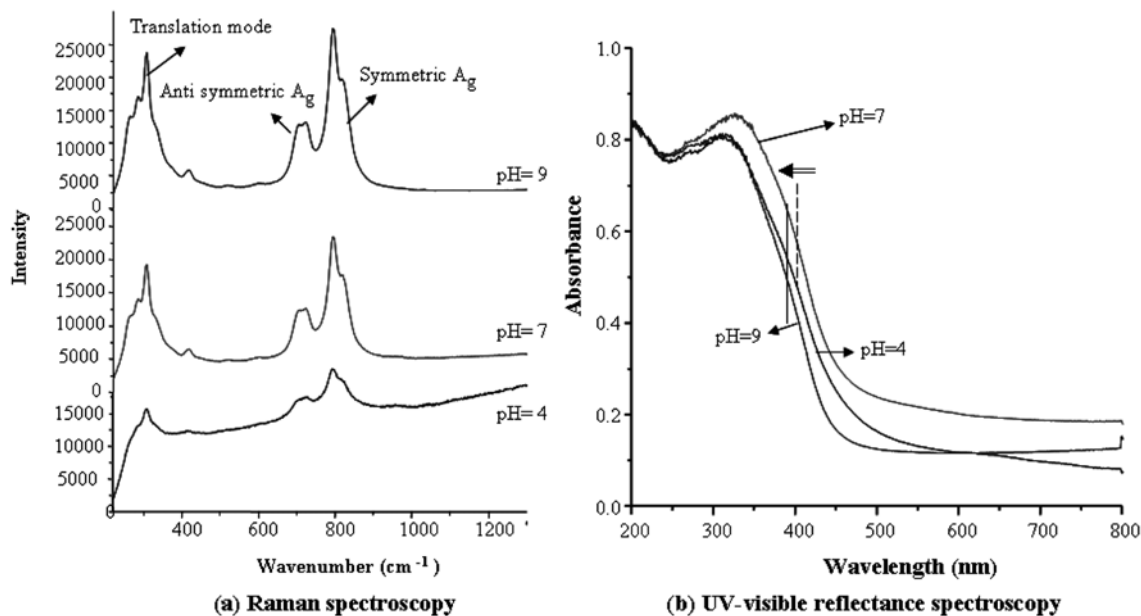


Fig. 2. The Raman spectroscopy (a) and UV-visible spectroscopy (b) of  $\text{Bi}_2\text{WO}_6$  prepared at different pH conditions.

Table 1. The conductivity and composition over a  $\text{Bi}_2\text{WO}_6/\text{PET}$  film's surface

Sample	Composition of film surface (atomic ratio)			Film thickness for 1 time coating (nm)	Transmittance at 450-550 nm (%)	Conductivity (ohm per square)
	Bi	W	O			
pH=4 (Bi/W=2.17)	21.95	10.10	67.96	150 nm	87	$1.0 \times 10^6$
pH=7 (Bi/W=2.12)	18.74	8.82	72.44	350 nm	85	$2.0 \times 10^6$
pH=9 (Bi/W=2.23)	20.48	9.16	70.36	450 nm	84	$2.0 \times 10^8$

more regular structure [12]. Therefore, it was concluded that the  $\text{Bi}_2\text{WO}_6$  particles synthesized here had a very regular, orthorhombic structure. The UV-visible spectra of the  $\text{Bi}_2\text{WO}_6$  powders in Fig. b) showed absorption at 380 and 400 nm in samples prepared in basic and acidic solutions, respectively. As generally the band gaps of a semiconductor material are closely related to the wavelength range absorbed and the higher the absorption wavelength, the shorter the band gap, it is postulated that the  $\text{Bi}_2\text{WO}_6$  samples prepared in acidic or neutral solutions had a shorter band gap than that of the sample prepared in basic solution. Here, the band gap decreased in the order  $\text{pH } 9 > \text{pH } 4 > \text{pH } 7$ , suggesting that the sample prepared in neutral solution has better conductivity than the other samples.

## 2. Conductivity of $\text{Bi}_2\text{WO}_6/\text{PET}$ Film

The conductivity and composition of the surface of the  $\text{Bi}_2\text{WO}_6/\text{PET}$  films after 1-coating cycle is summarized in Table 1. The true atomic molar ratios determined by EDS of Bi/W in the  $\text{Bi}_2\text{WO}_6/\text{PET}$  film surfaces were 2.17/1, 2.12/1, and 2.23/1 for the samples prepared in the pH 4, 7, and 9 solutions, respectively, indicating that Bi atoms are more easily incorporated into the  $\text{Bi}_2\text{WO}_6$  framework than W atoms. The amount of oxygen incorporated in the  $\text{Bi}_2\text{WO}_6$  framework was largest in the sample prepared at pH 7, proven to be important by its correlation here with the high conductivity of the sample.  $\text{Bi}_2\text{WO}_6/\text{PET}$  films with a single coating had different thicknesses depending upon the particle size applied, but the transmittances in the visible range were very similar, about 85%. The conductivity of the  $\text{Bi}_2\text{WO}_6/\text{PET}$  films prepared at pH 7 expressed

as the surface resistance per unit area,  $2.0 \times 10^6$  ohm/square, was better than that of the samples prepared at pH 4 ( $1.0 \times 10^6$  ohm/square) and pH 9 ( $2.0 \times 10^8$  ohm/square). Conductivity generally depends strongly on film thickness with thicker film having higher conductivity. However, here surface properties differed by pH, and the surface changes determined by zeta potential variation in deionized water were +10, -15, and -25 mV in pH 4, 7, and 9, respectively. It can be supposed that electron transfer would be better at a surface with positive charge compared to one with negative charge and that the surface of coated film composed of larger particles was possibly cracked. However, the film appeared to very stably adhered to the PET surface, and clearance between particles was not observed in a sample prepared at pH 4. On the basis of these results, conductivity was superior in material prepared at pH 4, in spite of a decrease of film thickness, and conductivity was closely related to the pH used in the preparation.

The conductivity of the  $\text{Bi}_2\text{WO}_6/\text{PET}$  film prepared at neutral pH as a function of the annealing temperature and film thickness is shown in Fig. 3. The  $\text{Bi}_2\text{WO}_6$  samples were thermally treated at 400, 600, and 800 °C before being coated onto the PET film (Fig. 3a), and the film thickness was controlled to 750, 1,500, and 2,000 nm (Fig. 3b). As the annealing temperature increased when thickness was constant, conductivity expressed as the surface resistance decreased to  $1.0 \times 10^{11}$  ohm/square. The film thickness by coating cycle was increased when annealing temperature was held constant; the conductivity of the  $\text{Bi}_2\text{WO}_6/\text{PET}$  film increased to  $5.0 \times 10^5$  ohm/

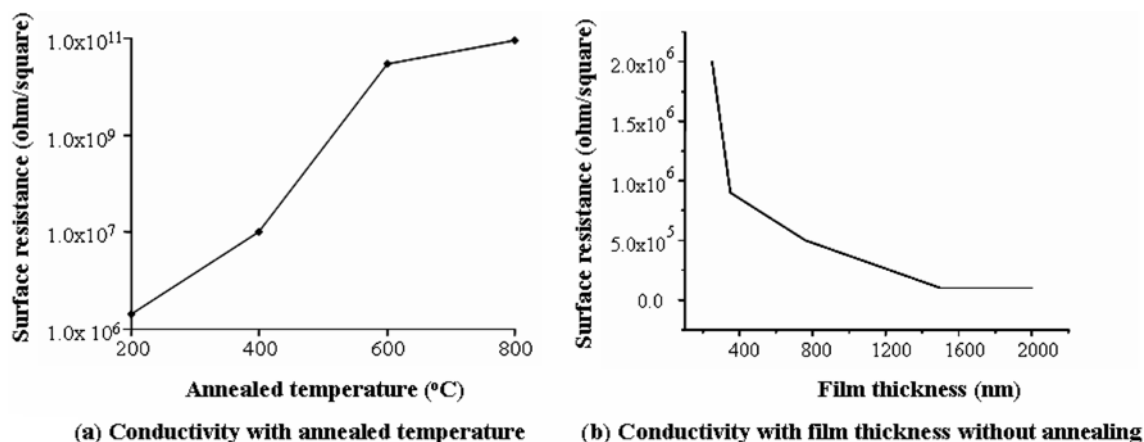


Fig. 3. The change of conductivity of Bi<sub>2</sub>WO<sub>6</sub>/PET film prepared at pH 7 with different annealed temperatures (a) and film thicknesses (b).

square. The film's transparency, however, decreased with an increase of film thickness, with the best transparency obtained after 2-coating cycles, having a thickness of 750 nm and a resistance of  $5.0 \times 10^4$  ohm/square. Consequently, we deduced from the results shown in Fig. 3a) that the optimum film thickness for obtaining a higher conductivity would be 1,500 nm; however, thicker films were not tested at this point.

### CONCLUSION

This study focused on determining the optimum conditions for obtaining PET films with high conductivity prepared by using Bi<sub>2</sub>WO<sub>6</sub> particles produced by a commercial hydrothermal method. The best conductivity was observed in a Bi<sub>2</sub>WO<sub>6</sub>/PET film prepared at pH 4 without any thermal treatment,  $1.0 \times 10^6$  ohm/square, expressed as surface resistance units. High temperature thermal treatment for the sample prepared at pH 7 was detrimental to the conductivity and the optimum film thickness for higher conductivity was about 1,500 nm. This study clearly demonstrates the need to control pH during Bi<sub>2</sub>WO<sub>6</sub> preparation to improve its conductivity.

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### REFERENCES

1. B. Frit and J. P. Mercurio, *J. Alloy. Compd.*, **188**, 27 (1992).
2. V. Sharma, A. K. Shukla and J. Gopalakrishnan, *J. Mater. Chem.*, **4**, 703 (1994).
3. S. Zhang, J. Shen, H. Fu, W. Dong, Z. Zheng and L. Shi, *J. Solid State Chem.*, **180**, 1456 (2007).
4. X. Zhao, T. Xu, W. Yao, C. Zhang and Y. Zhu, *Appl. Catal. B: Environ.*, **72**, 92 (2007).
5. A. M. Cruz and F. E. L. Rodriguez, *Mater. Res. Bull.*, **42**, 1851 (2007).
6. C.-Y. Hsieh and K.-Z. Fung, *J. Phys. Chem. Solids*, **69**, 302 (2008).
7. J. Yu, J. Xiong, B. Cheng, Y. Yu and J. Wang, *J. Solid State Chem.*, **178**, 1968 (2005).
8. H.-J. Jeon, M.-K. Jeon, M. Kang, S.-G. Lee, Y.-L. Lee, Y.-K. Hong and B.-H. Choi, *Mater. Lett.*, **59**, 1801 (2005).
9. M.-K. Jeon and M. Kang, *Mater. Lett.*, **62**, 676 (2008).
10. L. Zhou, W. Wang and L. Zhang, *J. Mol. Catal. A: Chem.*, **268**, 195 (2007).
11. H. Fu, C. Pan, L. Zhang and Y. Zhu, *Mater. Res. Bull.*, **42**, 696 (2007).
12. M. Crane, R. Forst, P. Williams and T. Klopogge, *J. Raman Spectrosc.*, **33**, 62 (2002).