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Selective Preparation of Monoclinic and Tetragonal $BiVO_4$ with Scheelite Structure and Their Photocatalytic Properties

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$BiVO_4$ powder with scheelite structure was obtained by hydrolyzing a nitric acid solution of $Bi(NO_3)_3$ and Na_3VO_4 with bases (Na_2CO_3 and $NaHCO_3$) at room temperature. Tetragonal $BiVO_4$ of a high-temperature form was obtained after 4.5 h of preparation time while monoclinic $BiVO_4$ was done after 46 h. Although the structure and the band gap of tetragonal $BiVO_4$ with scheelite structure were similar to those of monoclinic $BiVO_4$, the photocatalytic activity of the tetragonal $BiVO_4$ for O_2 evolution from an aqueous $AgNO_3$ solution under visible light irradiation was negligible. In contrast, the monoclinic $BiVO_4$ showed high photocatalytic activity. Distortion of a Bi−O polyhedron by a $6s^2$ lone pair of Bi^{3+} plays an important role for high photocatalytic activity of the monoclinic $BiVO_4$ under visible light irradiation.

1. Introduction

$BiVO_4$ has attracted attention as a ferroelastic and ion conductive material.[1−17] These properties strongly depend on the crystal form. $BiVO_4$ has three main crystal forms as shown in Figure 1: zircon structure with tetragonal system (z−t) and scheelite structure with monoclinic (s−m) and tetragonal (s−t) systems.[2,6] When $BiVO_4$ (z−t) is heat-treated above 670−770 K, $BiVO_4$ (s−m) is obtained. The phase transition is also observed at room temperature by crushing the powder.[10] The phase transition between $BiVO_4$ (s−m) and $BiVO_4$ (s−t) reversibly occurs at 528 K.[6] The change in the elastic properties by this phase transition has been widely studied.

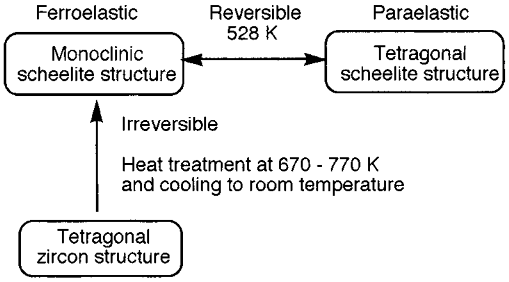

Figure 1. Phase transitions of $BiVO_4$.

$BiVO_4$ (s−m) is usually obtained by solid state and melting reactions at high temperature.[2,18,19] $BiVO_4$ (z−t) is prepared by a precipitation method from a $Bi(NO_3)_3$ nitric acid solution and an aqueous NH_4VO_3 solution at room temperature.[10,20] The authors have recently reported that crystalline $BiVO_4$ (s−m) and $BiVO_4$ (z−t) powder are selectively synthesized in aqueous media at room temperature under ambient pressure by reactions of layered potassium vanadates ($K_3V_5O_{14}$ and KV_3O_8) with $Bi(NO_3)_3$.[21] The band gaps of $BiVO_4$ (s−m) and $BiVO_4$ (z−t) were 2.4 and 2.9 eV, respectively. This $BiVO_4$ (s−m) powder showed high activity for photocatalytic O_2 evolution from aqueous $AgNO_3$

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(1) David, W. I. F.; Wood, I. G. *J. Phys. C: Solid State Phys.* **1983**, *16*, 5149.

(2) Lim, A. R.; Choh, S. H.; Jang, M. S. *J. Phys.: Condens. Matter* **1995**, *7*, 7309.

(3) Manolikas, C.; Amelinckx, S. *Phys. Status Solidi A* **1980**, *60*, 167.

(4) Akimov, S. V.; Mnushkina, I, E.; Dudnik, E. F. *Sov. Phys. Technol. Phys.* **1982**, *27*, 500.

(5) Hirota, K.; Komatsu, G.; Yamashita, M.; Takemura, H.; Yamaguchi, O. *Mater. Res. Bull.* **1992**, *27*, 823.

(6) Bierlein, J. D.; Sleight, A. W. *Solid State Commun.* **1975**, *16*, 69.

(7) Pinczuk, A.; Welber, B.; Dacol, F. H. *Solid State Commun.* **1979**, *29*, 515.

(8) David, W. I. F.; Glazer, A. M. *Phase Trans.* **1979**, *1*, 155.

(9) Manolikas, C.; Americkx, S. *Phys. Status Solidi A* **1980**, *60*, 167.

(10) Bhattacharya, A. K.; Mallick, K. K.; Hartridge, A. *Mater. Lett.* **1997**, *30*, 7.

(11) Mariathasan, J. W. E.; Hazen, R. M.; Finger, L. W. *Phase Trans.* **1986**, *6*, 165.

(12) (a) Lim, A. R.; Choh, S. H.; Jang, M. S. *Ferroelectrics* **1989**, *94*, 389. (b) Lim, A. R.; Chang, J.-H.; Choh, S. H. *Phys. Status Solidi B* **1996**, *196*, 33.

(13) (a) Yeom, T. H.; Choh, S. H.; Du, M. L. *J. Phys.: Condens. Matter* **1993**, *5*, 2017. (b) Yeom, T. H.; Rudowicz, C.; Choh, S. H. *Ferroelectrics* **1994**, *156*, 249. (c) Yeom, T. H.; Choh, S. H.; Du, M. L.; Jang, M. S. *Phys. Rev. B* **1996**, *53*, 3415. (d) Yeom, T. H.; Rudowicz, C.; Choh, S. H.; Mcgavin, D. G. *Phys. Status Solidi B* **1996**, *198*, 839.

(14) Man, P. P.; Choh, S. H.; Fraissard, *J. Solid State Nucl. Magn. Reson.* **1994**, *3*, 23.

(15) Choh, S. H. Z. *Natureforsch.* **1996**, *51a*, 591.

(16) Bodart, P. R.; Dumazy, Y.; Amoureux, J. P.; Fernandez, C. *Magn. Reson. Chem.* **1999**, *37*, 223.

(17) Jeong, H. T.; Jeong, S. Y.; Kim, W. T.; Kim, D. H. *J. Phys. Soc. Jpn.* **2000**, *69* (2), 306.

(18) Roth, R. S.; Waring, J. L. *Am. Mineral.* **1963**, *48*, 1348.

(19) Sleight, A. W.; Chen, H.-y.; Ferretti, A.; Cox, D. E. *Mater. Res. Bull.* **1979**, *14*, 1571.

(20) *Natl. Bur. Stand. Monogr. U.S.* **1964**, *25, Sec. 3*, 14.

(21) Kudo, A.; Omori, K.; Kato, H. *J. Am. Chem. Soc.* **1999**, *121*, 11459.

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solutions under visible light irradiation while the photocatalytic activity of $BiVO_4$ (z–t) was low. Thus, the photophysical and the photocatalytic properties of $BiVO_4$ (s–m) were quite different from those of $BiVO_4$ (z–t). Moreover, the $BiVO_4$ (s–m) powder prepared by this aqueous process at room temperature showed higher activity by 1 order of magnitude than that prepared by a solid-state reaction at 1170 K.[21,22] Thus, the usefulness of an aqueous process in a photocatalyst synthesis was demonstrated.

Crystal structure of $BiVO_4$ (s–m) is similar to that of $BiVO_4$ (s–t) because they possess scheelite structure. However, the Bi–O polyhedron in the $BiVO_4$ (s–m) is more distorted by a $6s^2$ lone pair of Bi^{3+} than that of $BiVO_4$ (s–t) as shown in Table 1.[8,12,19] On the other hand, $BiVO_4$ (s–m) consists of the same elements and the composition as $BiVO_4$ (s–t). Therefore, it is important to compare the photocatalytic properties of $BiVO_4$ (s–m) with $BiVO_4$ (s–t) to investigate the factor that affects photocatalytic activities. However, the preparation method of $BiVO_4$ (s–t) by an aqueous process at room temperature has not been developed.

In the present paper, a new preparation method of $BiVO_4$ with scheelite structure, especially a tetragonal system of a high-temperature form, in an aqueous media is reported. The factor affecting photocatalytic properties is discussed by the comparison of photophysical and photocatalytic properties of $BiVO_4$ (s–m) with those of $BiVO_4$ (s–t).

2. Experimental Section

$BiVO_4$ was synthesized in an aqueous media at room temperature under ambient pressure. $Bi(NO_3)_3{\cdot}5H_2O$ (Kanto Chemical, purity; 99.9%) and $Na_3VO_4{\cdot}7H_2O$ (Soekawa, purity; 99.9%) were dissolved in concentrated HNO_3, respectively. Nitric acid solutions of 0.12 mol/L $Bi(NO_3)_3$ and 0.12 mol/L Na_3VO_4 were prepared by adding water in those solutions. The concentration of the nitric acid was 2 mol/L at this time. After these nitric acid solutions of $Bi(NO_3)_3$ and Na_3VO_4 were mixed, a base (Na_2CO_3 or $NaHCO_3$) was added and the solution was stirred for 4.5–46 h. The $BiVO_4$ precipitation formed by the hydrolysis was washed by water, filtered, and dried at 320 K for 12 h. X-ray diffraction (RIGAKU; RINT-1400), diffuse reflectance spectra (JASCO; Ubest V-570), and scanning electron microscopy (Hitachi; S-5000) measurements were performed.

Photocatalytic O_2 evolution from an aqueous silver nitrate solution was carried out in a closed gas circulation system. The catalyst powder (1 g) was dispersed by a magnetic stirrer in an aqueous $AgNO_3$ solution (0.05 mol/L, 320 mL) in a reaction cell made of Pyrex glass. The light source was an ozone-free 300-W Xe illuminator (Ushio-CERMAX, LX300). Cutoff and band-pass filters (Kenko, L-42 ($\lambda > 420$ nm) and U-340 ($300 < \lambda < 380$ nm)) were employed for visible and UV irradiation, respectively. Amounts of evolved O_2 were determined using gas chromatography (Shimadzu, GC-8A, TCD, Ar carrier).

3. Results

(a) Effects of Bases Used for Hydrolyses on Crystal Forms and Photocatalytic Properties of $BiVO_4$. The effects of Na_2CO_3 and $NaHCO_3$ used for hydrolyses of the nitric acid solution of $Bi(NO_3)_3$ and Na_3VO_4 in the preparation of $BiVO_4$ on the photocatalytic activities for O_2 evolution from aqueous $AgNO_3$ solutions under visible light irradiation are shown in Table 2. The obtained crystal form of $BiVO_4$ was a monoclinic scheelite structure. Thus, a new aqueous process for the preparation of $BiVO_4$ (s–m) at room temperature in an aqueous medium was developed. $BiVO_4$ (s–m) obtained by using 7 g of Na_2CO_3 showed the highest photocatalytic activity. Hereafter, the preparation of $BiVO_4$ was performed at this best amount of Na_2CO_3.

Table 1. Cell Parameters and Bond Lengths of $BiVO_4$ with Scheelite Structure[19]

crystal system	cell parameter				bond length/Å	
	a	*b*	*c*	β	Bi–O	V–O
monoclinic	5.193	5.090	11.697	90.4	2.354 ×2	1.69 ×2
					2.372 ×2	1.77 ×2
					2.516 ×2	
					2.628 ×2	
tetragonal	5.147	5.147	11.722	90.0	2.453 ×4	1.72 ×4
					2.499 ×4	

Table 2. Effects of Base Used for Preparation on the Photocatalytic Oxygen Evolution from Aqueous $AgNO_3$ Solutions (0.05 mol/L, 320 mL) under Visible Light Irradiation ($\lambda > 420$ nm) on $BiVO_4$ with Monoclinic Scheelite Structure[a]

added base	amount of base added/g	rate of O_2 evolution/mol·h^{-1}
Na_2CO_3	3	34
	5	26
	6	61
	7	226
	8	43
	10	22
$NaHCO_3$	3	27
	5	31
	7	26
	8	58

[a] Starting solution: 0.12 mol/L $Bi(NO_3)_3$ (80 mL) and 0.12 mol/L Na_3VO_4 (80 mL) in 2 mol/L of nitric acid solution, preparation time: 46 h. The experimental error in the rate of O_2 evolution of the photocatalytic activity was within ≈10%.

(b) Formation Process of $BiVO_4$. To investigate the formation process of $BiVO_4$, X-ray diffraction patterns of $BiVO_4$ obtained at 4.5–46 h of different preparation time were measured as shown in Figure 2A,B. The difference in the XRD patterns between $BiVO_4$ (s–m) and $BiVO_4$ (s–t) can be judged by the existence of a peak at 15° and splitting of peaks at 18.5°, 35°, and 46° of 2θ. The pure pattern of $BiVO_4$ (s–t) was observed after 4.5 h while the pattern of $BiVO_4$ (s–m) was observed in addition to the pattern of $BiVO_4$ (s–t) after 9 and 24 h. The pattern of $BiVO_4$ (s–m) was finally obtained after 46 h. Thus, $BiVO_4$ (s–t) was formed at the first stage and then it was converted to a monoclinic phase. This result indicates that $BiVO_4$ (s–m) and $BiVO_4$ (s–t) were able to be selectively synthesized by adjusting the preparation time.

Scanning electron microscope measurements of $BiVO_4$ prepared at 4.5–46 h of preparation time were carried out. $BiVO_4$ (s–t) powder formed after 4.5 h was a spherical particle with about 2 μm of a particle size and the particles aggregated as shown in Figure 3A. The particle size of $BiVO_4$ formed after 24 h was about 1 μm and the crystallinity of the particles became better (Figure 3B). $BiVO_4$ powder formed after 46 h was well-crystallized and some particles possessed a plate shape with about 0.2–1 μm of particle sizes (Figure 3C). Thus, the particle size became small and the shape and crystallinity of the particle were also changed as the preparation time was long.

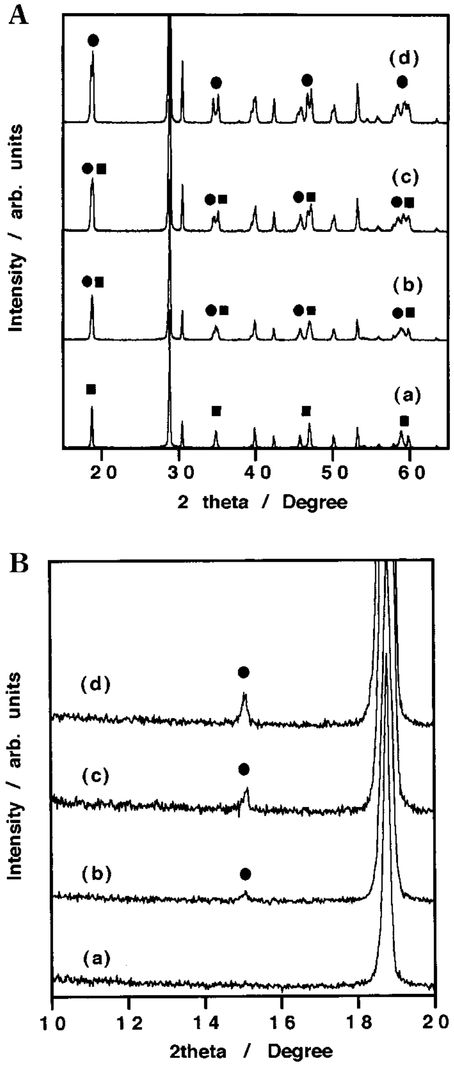

Figure 2. (A) and (B) XRD patterns of $BiVO_4$ prepared at different preparation times: (a) after 4.5 h, (b) 9 h, (c) 24 h, and (d) 46 h. Closed circles and squares indicate the representative peaks of $BiVO_4$ (s−m) and $BiVO_4$ (s−t), respectively. The starting solution was a mixture of 0.12 mol/L $Bi(NO_3)_3$ and Na_3VO_4 of nitric solution (2 mol/L) and Na_2CO_3 (7 g).

The X-ray diffraction pattern of the product obtained by dispersing $BiVO_4$ (s−t) powder in water was compared with that in an aqueous nitric acid solution whose pH was equal to the preparation solution ($\approx$ 0.1) to examine the reason for the phase transition from $BiVO_4$ (s−t) to $BiVO_4$ (s−m) during the preparation as shown in Figure 4. The samples were dispersed using a magnetic stirrer for 2 days. $BiVO_4$ (s−t) was not converted in water, indicating the phase transfer was not due to the mechanical process as observed for the phase transition from $BiVO_4$ (z−t) to $BiVO_4$ (s−m) by crushing the powder.[10] In contrast, $BiVO_4$ (s−t) was converted to $BiVO_4$ (s−m) in a nitric acid. This result suggests that the dissolution and subsequent recrystallization occurring in the low pH solution contribute to the formation of $BiVO_4$ (s−m) from $BiVO_4$ (s−t).

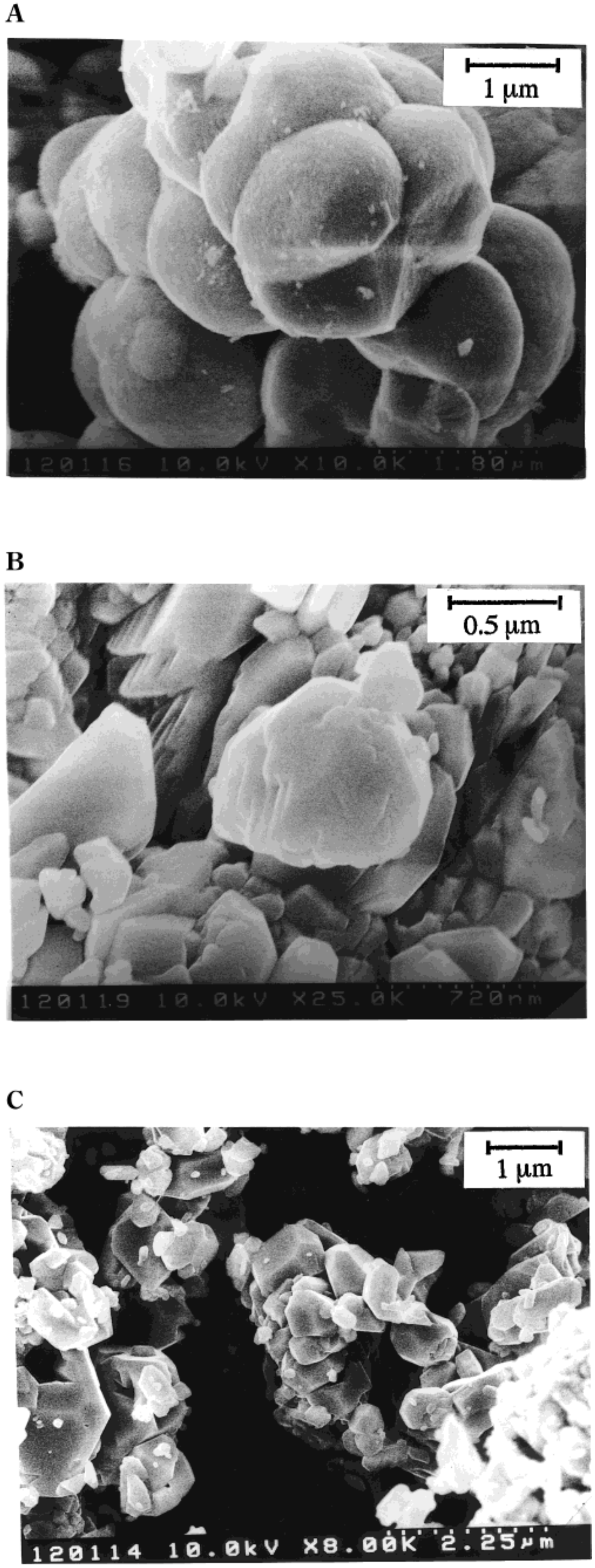

Figure 3. SEM photographs of $BiVO_4$ prepared at different preparation times: (A) after 4.5 h, (B) 24 h, and (C) 46 h.

(c) Comparison in Photophysical and Photocatalytic Properties between $BiVO_4$ (s−m) and $BiVO_4$ (s−t). Diffuse reflectance spectra of $BiVO_4$ (s−m) and $BiVO_4$ (s−t) are shown in Figure 5. $BiVO_4$ (s−t) was murky yellow while $BiVO_4$ (s−m) was vivid yellow. The absorption edges observed in a visible light region did not have much difference between $BiVO_4$ (s−t) and $BiVO_4$ (s−m). The diffuse reflectance spectrum

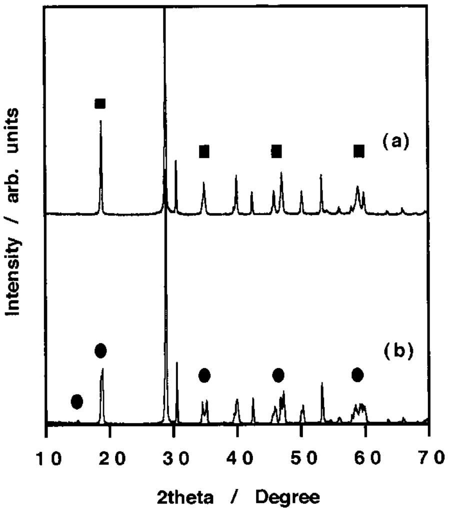

Figure 4. XRD patterns of the products obtained from BiVO$_4$ (s−t) treated in (a) water and (b) HNO$_3$ for 2 days. Closed circles and squares indicate the representative peaks of BiVO$_4$ (s−m) and BiVO$_4$ (s−t), respectively.

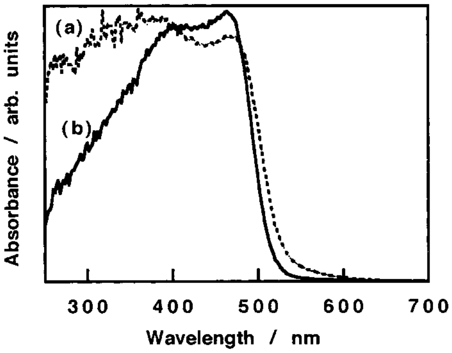

Figure 5. Diffuse reflectance spectra of (a) BiVO$_4$ (s−t) and (b) BiVO$_4$ (s−m).

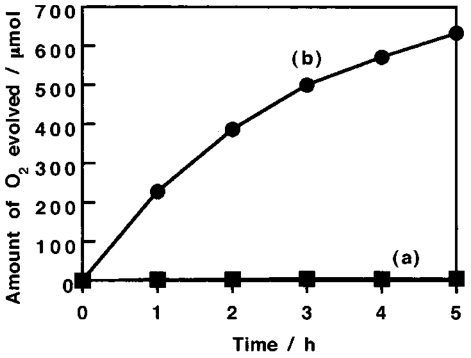

Figure 6. Photocatalytic O$_2$ evolution from aqueous AgNO$_3$ solutions (0.05 mol/L, 320 mL) under visible light irradiation ($\lambda > 420$ nm) on (a) BiVO$_4$ (s−t) and (b) BiVO$_4$ (s−m).

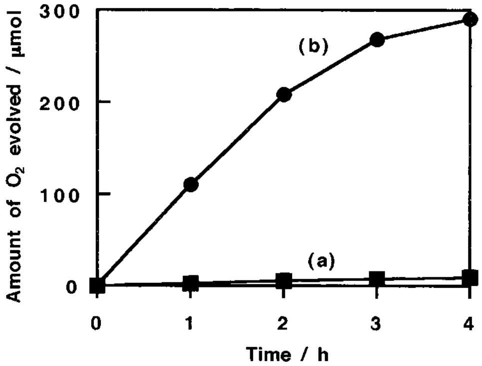

Figure 7. Photocatalytic O$_2$ evolution from aqueous AgNO$_3$ solutions (0.05 mol/L, 320 mL) under ultraviolet light irradiation ($300 < \lambda < 380$ nm) on (a) BiVO$_4$ (s−t) and (b) BiVO$_4$ (s−m).

of this BiVO$_4$ (s−m) was in agreement with that synthesized by an aqueous process reported before.[21] The onset wavelengths of the diffuse reflectance spectra indicated that the band gaps of BiVO$_4$ (s−m) and BiVO$_4$ (s−t) were 2.41 and 2.34 eV, respectively. The absorption band in the UV light region ($\lambda \approx 300$ nm) observed for BiVO$_4$ (s−t) was larger than that for BiVO$_4$ (s−m).

Photocatalytic activities for O$_2$ evolution from aqueous silver nitrate solutions on BiVO$_4$ (s−m) and BiVO$_4$ (s−t) under visible light irradiation ($\lambda > 420$ nm) and under UV light irradiation ($300 < \lambda < 380$ nm) are shown in Figures 6 and 7, respectively. Although the absorption band of BiVO$_4$ (s−m) in the visible light region was similar to that of BiVO$_4$ (s−t), BiVO$_4$ (s−m) showed higher photocatalytic activity than BiVO$_4$ (s−t). Moreover, the photocatalytic activity of BiVO$_4$ (s−t) was negligible, even under UV light irradiation. The high activity of BiVO$_4$ (s−m) is probably due to the distortion of the Bi−O polyhedron as shown in Table 1 because the major difference between BiVO$_4$ (s−m) and BiVO$_4$ (s−t) is only the distortion.

It has been reported that BiVO$_4$ (z−t) with a 2.9-eV band gap showed the activity for the photocatalytic O$_2$ evolution under UV light irradiation, but it was low under visible light irradiation.[21] Thus, the difference in the photophysical and photocatalytic properties among BiVO$_4$ with three kinds of crystal structures has been clarified. It should be stressed that the photophysical and photocatalytic properties of BiVO$_4$ (s−t) of a high-temperature form were able to be measured at room temperature by the development of the present preparation method at room temperature.

4. Discussion

(a) Factors Affecting the Selective Preparation of BiVO$_4$ (s−m) and BiVO$_4$ (s−t). It was revealed from XRD and SEM measurements (Figures 2 and 3) that BiVO$_4$ (s−t) powder with a large particle size was observed at the initial stage of the preparation. The particle size became small with the preparation time. Finally, BiVO$_4$ (s−m) powder with a small particle size and good crystallinity was obtained. This process is considered as follows. Although the BiVO$_4$ (s−m) is thermodynamically more stable than BiVO$_4$ (s−t) at room temperature, the formation of BiVO$_4$ (s−t) seems to be preferable kinetically by a sudden increase in pH by adding a base. BiVO$_4$ (s−t) with a large particle size does not phase-transform to the thermodynamically stable BiVO$_4$ (s−m) at room temperature. The particle size became smaller during the preparation reaction with dissolution and recrystallization. BiVO$_4$ (s−m) is finally formed at the recrystallization and/or in the small particles in which the stress can easily be released.

(b) The Reason for the Difference in the Photocatalytic Activity between BiVO$_4$ (s−m) and BiVO$_4$ (s−t). Sleight et al. have reported the structural analysis of BiVO$_4$ (s−m) and BiVO$_4$ (s−t).[6,8,12,18,19] The variety of the bond length of Bi−O as shown in Table 1 indicates that $BiVO_4$ (s−m) is greatly distorted compared with $BiVO_4$ (s−t). This distortion is due to $6s^2$ lone pairs of Bi^{3+}. Such effects of the $6s^2$ lone pair have been reported for some bismuth oxide compounds.[23,24] The difference in the distortion leads to the fact that $BiVO_4$ (s−t) is paraelastic whereas $BiVO_4$ (s−m) is ferroelastic. In the present study, it was found that the photocatalytic activity was also changed by the difference between monoclinic and tetragonal systems as well as the elastic properties, even if they possessed the same scheelite structure. This indicates that the distortion of the metal−oxygen polyhedron is an important factor affecting photocatalytic properties. Inoue et al. have reported the effect of the local polarization due to the distortion of the TiO_6 octahedron of various titanates on their photocatalytic properties.[25,26] The factors affecting photocatalytic properties have also been discussed by comparing the photocatalytic activity of $Sr_2Ta_2O_7$ with that of $Sr_2Nb_2O_7$ with a layered perovskite structure.[27] However, when the structure and composition of photocatalyst materials are different from each other, the energy structure such as a conduction band potential also affects photocatalytic properties, resulting in the complicated factors. In contrast to their materials, the composition, elements, and the crystal structure of $BiVO_4$ (s−m) are the same as those of $BiVO_4$ (s−t) except for the distortion. Furthermore, the energy structure of $BiVO_4$ (s−m) is also similar to that of $BiVO_4$ (s−t) judging from DRS. The major difference between $BiVO_4$ (s−m) and $BiVO_4$ (s−t) is the distortion of the Bi−O polyhedron by $6s^2$ lone pairs of Bi^{3+}. Therefore, it was concluded that this distortion dominantly affects the photocatalytic properties of scheelite $BiVO_4$. This is also important for the consideration of the visible light response of the $BiVO_4$ photocatalyst. The distortion probably affects the charge separation and delocalization of photogenerated electrons and holes.

5. Conclusion

(1) A new aqueous process at room temperature at ambient pressure for the preparation of $BiVO_4$ was found. It is characteristic of this method that $BiVO_4$ (s−m) and $BiVO_4$ (s−t) were selectively prepared by adjusting the preparation time. By this method, $BiVO_4$ (s−t) of a high-temperature form was obtained at room temperature.

(2) The band gap of $BiVO_4$ (s−m) (2.41 eV) was similar to that of $BiVO_4$ (s−t) (2.34 eV), suggesting the energy structures were similar to each other. However, $BiVO_4$ (s−m) showed high activity for photocatalytic O_2 evolution under visible light irradiation while the activity of $BiVO_4$ (s−t) was negligible.

(3) The importance of $6s^2$ lone pairs of Bi^{3+} as a factor affecting photocatalytic properties of $BiVO_4$ was clarified by a comparison of the photocatalytic properties of $BiVO_4$ (s−m) with $BiVO_4$ (s−t).

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(22) Kudo, A.; Ueda, K.; Kato, H.; Mikami, I. *Catal. Lett.* **1998**, *53*, 229.

(23) Jakubowicz, N.; Pérez, O.; Grebille, D.; Leligny, H. *J. Solid State Chem.* **1998**, *139*, 194.

(24) Giraud, S.; Wignacourt, J.-P.; Drache, M.; Nowogrocki, G.; Steinfink, H. *J. Solid State Chem.* **1999**, *142*, 80.

(25) Inoue, Y.; Kubokawa, T.; Sato, K. *J. Phys. Chem.* **1991**, *95*, 4059.

(26) Ogura, S.; Kohno, M.; Sato, K.; Inoue, Y. *Appl. Surf. Sci.* **1997**, *121/122*, 521.

(27) Kudo, A.; Kato, H.; Nakagawa, S. *J. Phys. Chem.* **2000**, *104*, 571.