288

Preparation and Characterization of $Ca_4Bi_6O_{13}$ Complex Oxide

Kenji Obata,[1] Kensuke Matsumoto,[1] Takuya Uehara,[1] Akane Doi,[1] Yuki Obukuro,[1] and Shigenori Matsushima*[1,2]

[1]*Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology,*
5-20-1 Shii, Kokuraminami-ku, Kitakyushu, Fukuoka 802-0985

[2]*Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology,*
Kitakyushu Science and Research Park, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0196

(Received October 22, 2010; CL-100901; E-mail: smatsu@kct.ac.jp)

A single phase of $Ca_4Bi_6O_{13}$ crystal was obtained at lower calcination temperature in a citric acid complex method than in a solid-state reaction. From the diffuse reflection spectra, it was found that $Ca_4Bi_6O_{13}$ is direct-gap material and that the optical band gap is 2.92 eV. After heating at 600 °C or above, the specific surface area of $Ca_4Bi_6O_{13}$ powder was ca. three times larger when prepared by a citric acid complex method than by solid-state reaction. Further, it was confirmed that the photocatalytic activity of $Ca_4Bi_6O_{13}$ for the degradation of Methylene Blue (MB) was higher in a citric acid complex method than in a solid-state reaction under visible-light irradiation ($\lambda \geq 420$ nm).

Recently, $Ca_4Bi_6O_{13}$ has attracted considerable attention as a new photocatalyst because of the small band gap energy. However, $Ca_4Bi_6O_{13}$ powder has been prepared by a solid-state reaction until now.[1] Although solid-state reaction is most frequently used because of easiness and convenience, this method has several problems, such as crystal growth, change of the stoichiometric ratio, and easiness of formation of the secondary phase. This is because the grinding and the calcination of starting materials must be repeated many times to prepare intended crystal phase. As a result, the surface area of the product decreases and the catalytic activity inevitably falls. Marcilly et al. have reported a new preparation method employing organic acids (citric, malic, tartaric, glycolic acids, etc.) to obtain metal oxides.[2] They showed that H^+ in an organic acid with –OH or –COOH groups is replaced by the metal ion in the solution and that the citric acid complex is easily formed. This complex is available for a precursor to prepare the objective material. Thus, it is expected that the precursor is transformed to objective oxide at lower calcination temperature than the case of a solid-state reaction that and the resulting final product has a large surface area and a high homogeneity.

In the present study, we have examined preparation of $Ca_4Bi_6O_{13}$ powder with high specific surface area by a citric acid complex, instead of a solid-state reaction, and characterized by using an X-ray diffractometer, a UV–vis spectrometer, and a surface-area measuring instrument. Further, the photocatalytic activities for degrading Methylene Blue (MB) over $Ca_4Bi_6O_{13}$ prepared from a citric acid complex and solid-state were compared.

$Ca_4Bi_6O_{13}$ powder was synthesized by a citric acid complex and a conventional solid-state reaction. For the citric acid complex, $Ca(NO_3)_2 \cdot 4H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, and citric acid in a 2:3:5 molar ratio were dissolved in 3 M HNO_3. The citric acid used was equalized to the whole amount of metal ions. The solution was dehydrated at 70 °C until a sol was obtained. The sol was heated on a hot plate to prepare the precursor powder of $Ca_4Bi_6O_{13}$. Then, the precursor was calcined at 600, 700, and

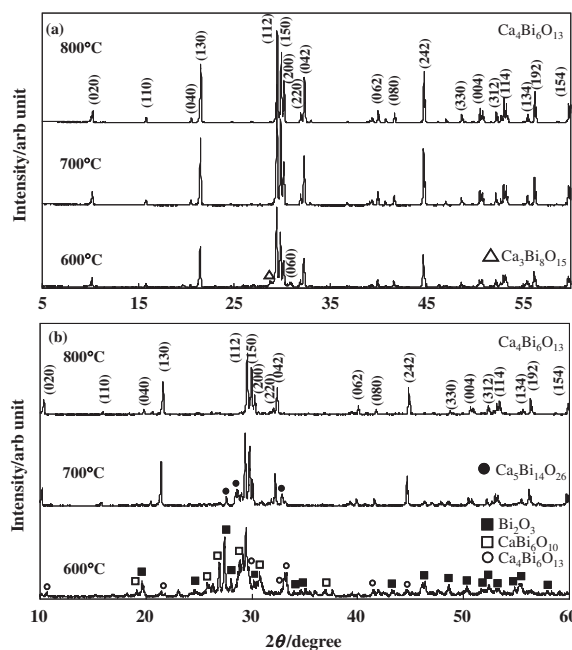**Figure 1.** XRD patterns of $Ca_4Bi_6O_{13}$ powders prepared from the citric acid complex (a) and the solid-state reaction (b).

800 °C for 12 h in air. On the other hand, $CaCO_3$ and $(BiO)_2CO_3$ as the starting materials were mixed in a 4:3 molar ratio in a solid-state reaction. The mixture was also calcined at 600, 700, and 800 °C for 12 h in air. The heating ratio was set to 10 °C min^{-1} in all cases.

Figures 1a and 1b show the XRD patterns of sample powders prepared from the citric acid complex and the solid-state reaction. These powders were calcined at 600, 700, and 800 °C in air for 12 h. In the citric acid complex method, a small amount of $Ca_3Bi_8O_{15}$ as impurity was observed in addition to $Ca_4Bi_6O_{13}$ phase at 600 °C. After the mixture was heated at 700 °C or above, the impurities vanished and a single phase of $Ca_4Bi_6O_{13}$ appeared. On the other hand, a mixture phase consisting of $CaBi_6O_{10}$, $Ca_5Bi_{14}O_{26}$, and Bi_2O_3 was confirmed at 600 °C in the solid-state reaction. When the mixture was calcined at 800 °C, those impurities disappeared and a single phase of $Ca_4Bi_6O_{13}$ was formed. From the comparison of Figures 1a and 1b, it is clear that the temperature that the single phase of $Ca_4Bi_6O_{13}$ appears in the citric acid complex method is about 100 °C lower than that of the solid-state reaction method.

The Brunauer–Emmett–Teller (BET) surface areas for $Ca_4Bi_6O_{13}$ powder was estimated from nitrogen adsorption isotherms in the relative pressure range of $0.1 < p/p_0 < 0.3$.[3,4] For the citric acid complex, the specific surface area of $Ca_4Bi_6O_{13}$ powder

Table 1. Specific surface area of $Ca_4Bi_6O_{13}$ by BET method

Preparation method	Temperature /°C	Specific surface area /m² g⁻¹
Citric acid complex method	600	2.24
	700	1.05
	800	—[a]
Solid-state reaction method	600	0.78
	700	—[a]
	800	—[a]

[a]Below $0.01\,m^2\,g^{-1}$.
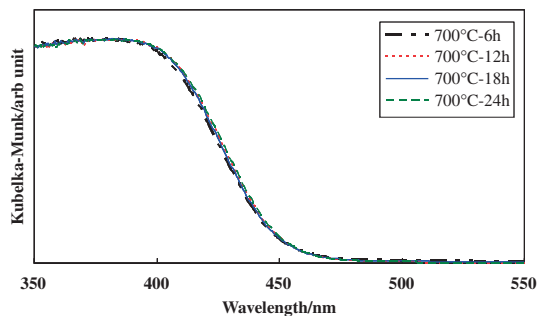
Figure 2. UV–vis diffuse reflectance spectra for the precursor calcined at 700 °C for various times.

calcined at 700 °C in air for 12 h was calculated to be $1.05\,m^2\,g^{-1}$, by applying a least-squares fit to a BET plot. In the case of a solid-state reaction, the $Ca_4Bi_6O_{13}$ powder calcined under the same conditions had an unmeasurable low value (below $0.01\,m^2\,g^{-1}$). Table 1 shows the specific surface areas of $Ca_4Bi_6O_{13}$ powder calcined at various temperatures. At 600 °C, the specific surface area is ca. three times larger in the citric acid complex method than in the solid-state reaction. The difference in the surface area between the two preparation methods expands at 700 °C as described above. In addition, a single phase of $Ca_4Bi_6O_{13}$ at 700 °C was obtained via the citric acid complex as seen from XRD measurements.

The UV–vis diffuse reflectance spectra for the precursor calcined at 700 °C for various times in air were collected in the wavelength range of 250 to 800 nm at room temperature. The measurement results are shown in Figure 2. The shifting of the onset of diffuse reflection spectra was not observed, although the calcination time of the precursor was extended up to 24 h. The optical band gap, E_g, of $Ca_4Bi_6O_{13}$ was estimated by using the Kubelka–Munk (KM) function eq 1 and the following eq 2. The KM function for the semi-infinite case can be described as follows:[5]

$$f(R_\infty) = (1 - R_\infty)^2/2R_\infty = \alpha/S \qquad (1)$$

where R_∞, α, and S are the diffuse reflectance from the sample, the absorption coefficient, and the scattering coefficient, respectively. The absorption coefficient, α, was determined by using the following equation:[6]

$$\alpha = A(h\nu - E_g)^n/h\nu \qquad (2)$$

where A, $h\nu$, and E_g are constant, the photon energy, and the optical band gap, respectively. In this equation, n depends on the nature of band transition, $n = 1/2$ for direct and $n = 2$ for indirect allowed transitions. If the scattering coefficient, S, does not
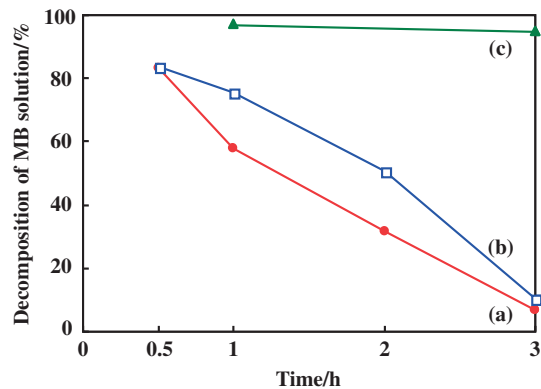
Figure 3. Decomposition of MB solution as a function of irradiation time under visible light ($\lambda \geq 420\,nm$): $Ca_4Bi_6O_{13}$ prepared from the citric acid complex (a), the solid-state reaction (b), and TiO_2 (c).

depend on the wavelength of the incident light, the KM function is directly proportional to the absorption coefficient. Thus, n may be evaluated from the slope of the straight line of $\ln f(R_\infty)h\nu$ vs. $\ln (h\nu - E_g)^n$. The best linearity was obtained in the case of $n = 1/2$, indicating that $Ca_4Bi_6O_{13}$ is direct-gap material. Further, the relationship between $\{f(R_\infty)h\nu\}^{1/n}$ and $h\nu$ was plotted, and a tangential line was drawn near the absorption edge. As the result, the optical band gap was estimated to be 2.92 eV from the x-intercept of the tangential line.

Subsequently, a $Ca_4Bi_6O_{13}$ pellet was used for the degradation of Methylene Blue (MB) under visible-light irradiation. The optical system consisted of a 500 W Xe arc lamp and a cut-off filter ($\lambda \geq 420\,nm$). The $Ca_4Bi_6O_{13}$ pellet was sunk in 10 mL of MB solution (5 ppm), and the degradated concentrations of MB were determined using an UV–vis spectrometer after visible light was irradiated. The photocatalytic activities were evaluated by the decrease of MB concentration after irradiation for 3 h. Figure 3 shows the concentration as a function of irradiation time over the photocatalyst. As a comparison, MB photodegradations over a $Ca_4Bi_6O_{13}$ pellet prepared from a solid-state reaction method and a TiO_2 (Degussa P-25) pellet were also carried out under the same conditions and are shown in Figure 3. Among the three kinds of photocatalysts examined, the highest activity is obviously achieved for $Ca_4Bi_6O_{13}$ prepared from the citric acid complex.

These results indicate that the citric acid complex method is a very promising procedure to prepare $Ca_4Bi_6O_{13}$ powder with single phase, high specific surface area, and high photocatalytic activity under visible-light irradiation.

References
1 B. Hallstedt, D. Risold, L. J. Gauckler, *J. Am. Ceram. Soc.* **1997**, *80*, 2629.
2 C. Marcilly, P. Courty, B. Delmon, *J. Am. Ceram. Soc.* **1970**, *53*, 56.
3 S. Brunauer, L. S. Deming, W. E. Deming, E. Teller, *J. Am. Chem. Soc.* **1940**, *62*, 1723.
4 S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309.
5 Y. I. Kim, S. J. Atherton, E. S. Brigham, T. E. Mallouk, *J. Phys. Chem.* **1993**, *97*, 11802.
6 H. Demiryont, J. R. Sites, *J. Vac. Sci. Technol., A* **1984**, *2*, 1457.