Preparation and photocatalytic properties of new calcium and lead bismuthates

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Two new pentavalent bismuthates, CaBi₂O₆·H₂O and PbBi₂O₆·H₂O were prepared from NaBiO₃·nH₂O. Broadened X-ray powder diffraction patterns for both bismuthates were indexed to the hexagonal cell observed for PbSb₂O₆-type SrBi₂O₆. The lattice parameters were a = 0.555(1) and c = 0.530(1) nm for CaBi₂O₆·1.1H₂O and a = 0.5544(4) and c = 0.531(1) nm for PbBi₂O₆·1.1H₂O. At elevated temperatures, the Ca derivative decomposed to Ca₂Bi₄O₁₂ and an unknown phase via the fluorite-type structure, whereas the Pb derivative changed to Pb₁₂Bi₂O₁₃ via the fluorite-type (Pb₁₂Bi₂O₃)O₄. Both Ca and Pb derivatives exhibited photocatalytic activity for the decomposition of phenol under visible light irradiation, although the adsorption of phenol was observed under dark conditions. The fluorite-type phases evolved from the Ca and Pb derivatives did not adsorb phenol under dark conditions, and their photocatalytic activities toward phenol decomposition under visible light were inferior to those of the parent compounds.

Key-words : Bismuthate, Photocatalysis, Pentavalent bismuth

1. Introduction

As oxides, bismuth atoms can adopt trivalent and pentavalent states. Some mixed valent bismuthes are superconductors, as observed in Ba(Bi, Pb)O₃ and (Ba, K)BiO₃. It is difficult to prepare pentavalent bismuthates through high temperature reactions, except for the system containing barium oxide: most bismuthates have trivalent bismuth atoms. Superconductive perovskite-type oxides, (Sr, A)BiO₃ (A = K, Rb), (K, Bi)BiO₃, and unique oxides with disproportionate valence states, e.g., Ag₂BiO₃ and BiNiO₃, have been reported elsewhere. Superconductive double perovskite-type bismuthates can be prepared from the same starting compound. Moreover, this starting compound could be used in ion-exchange reactions to yield SrBi₂O₆, BaBi₂O₆, and (Li, Na)BiO₃. Both SrBi₂O₆ and BaBi₂O₆ had PbSb₂O₆-type structures; the crystal structure refinement of SrBi₂O₆ was reported elsewhere.

In the course of the preparation of the new pentavalent bismuthates, we attempted to prepare the previously unreported CaBi₂O₆, CdBi₂O₆, and PbBi₂O₆ from NaBiO₃·nH₂O. We obtained the Ca and Pb derivatives for the first time by using molten salt and low temperature solution methods, respectively. The Cd derivative, prepared by hydrothermal reaction, had a PbSb₂O₆-type structure with ordering of the Cd and Bi atoms. We previously reported that ABi₂O₆ (A = Sr and Ba) exhibited photocatalytic activity for the decomposition of phenol under visible light irradiation. As the Ca and Pb derivatives had similar crystal structures to ABi₂O₆ (A = Sr and Ba), their photocatalytic behaviors were investigated. Here, we will describe the preparation and photocatalytic properties of these new pentavalent bismuthates.

2. Experimental

The Pb derivative was prepared by stirring NaBiO₃·nH₂O in Pb(NO₃)₂ solution [molar ratio; NaBiO₃·nH₂O:Pb(NO₃)₂ = 1:4] at 10°C for 5 d, and then filtering the product and washing with distilled water. The Ca analogue was synthesized by immersing NaBiO₃·nH₂O in a molten mixture of Ca(NO₃)₂·4H₂O and CaCl₂·2H₂O [NaBiO₃·nH₂O:Ca(NO₃)₂·4H₂O:CaCl₂·2H₂O = 1:1:1] at 200°C for 10 h. After cooling, excess nitrates and chlorides were dissolved with distilled water, and the solution and product were separated by filtration and washed with distilled water. SrBi₂O₆ and BaBi₂O₆ as reference samples were prepared from NaBiO₃·nH₂O, as described elsewhere.

The products were identified by X-ray powder diffraction using monochromated Cu Kα radiation. Thermal stabilities were investigated by TG-DTA with a heating rate of 10°C/min from room temperature to 800°C. For elemental composition analysis, the samples were completely dissolved in a mixture of HCl and HNO₃ at room temperature, and the amounts of bismuth, calcium and lead were determined by inductively coupled plasma spectroscopy. The sodium content was analyzed by atomic absorption spectrometry.

Ab initio calculations were performed on the basis of the plane-wave pseudopotential strategy using the VASP program (Vienna Ab Initio Simulation Package). The projector-augmented wave approach and a generalized gradient approximation of the PBE-type were used. An energy cutoff of 400 eV was chosen. The reported crystallographic data of tetragonal, trirutile-, and fluorite-type bismuthates were used as initial parameters. The volumes, shapes, and all atomic positions were allowed to change. k-point grids of 8 × 8 × 4 and 7 × 7 × 7 were auto-

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matically generated for the tetragonal and hexagonal cells, respectively.\textsuperscript{24)}

Diffuse reflectance spectra of the powder samples were measured with a JASCO V-550 spectrometer. The photocatalytic activity was examined for the decomposition of phenol (18 ppm solution) under visible light cutoff with 420 nm. The time dependence of phenol concentration was checked by liquid chromatography (JASCO LC-2000). For the first 60 min, the solution was stirred in the dark to examine phenol adsorption phenomena.

3. Results and discussion

3.1 Preparation of new Ca and Pb bismuthates

Similarly to other ABi$_2$O$_6$-type compounds (A: Mg, Zn, Sr, Ba), the preparations of CaBi$_2$O$_6$ and PbBi$_2$O$_6$ were attempted with NaBiO$_3$·nH$_2$O. However, the successful synthesis of these compounds required different conditions. The Ca derivative was obtained only by using a mixed molten salt at 200°C; pyrochlore-type compounds appeared under hydrothermal condition.\textsuperscript{12)} In the case of PbBi$_2$O$_6$, only a low temperature reaction in solution could produce the PbSb$_2$O$_6$-type phase; unknown multi-phases including transparent plate-like crystals appeared under hydrothermal conditions. The X-ray powder diffraction patterns of the Ca and Pb derivatives were broadened when compared with those of SrBi$_2$O$_6$ and BaBi$_2$O$_6$ (Fig. 1). The X-ray powder diffraction patterns of SrBi$_2$O$_6$ and BaBi$_2$O$_6$ could be indexed completely with the hexagonal cell of the PbSb$_2$O$_6$-type structure, despite the presence of a small amount of an impurity phase. The broadened X-ray powder diffraction pattern of the Pb derivative was also indexed with the hexagonal cell, and the calculated lattice parameters were $a = 0.5544(4)$ and $c = 0.531(1)$ nm. The X-ray powder diffraction pattern for the Ca analogue was most broadened among the various ABi$_2$O$_6$-type bismuthates, but could be approximately indexed with the hexagonal cell with $a = 0.555(1)$ and $c = 0.530(1)$ nm. The precise lattice parameters could not be determined because of the low number of diffraction peaks.

Mass losses were observed upon heating for both bismuthates, as shown in the TG curves in Fig. 2. The X-ray powder diffraction patterns of the products after heating at 200–800°C are shown in Fig. 3. For the Pb sample heated at 400°C, the X-ray powder diffraction patterns showed sharp diffraction peaks and could be indexed with the cubic cell. This phase was found to have the fluorite-type structure, and its crystal structure was refined successfully through the application of the neutron powder diffraction technique as reported elsewhere.\textsuperscript{19)} Finally, the Pb derivative was transformed to Pb$_1$Bi$_2$O$_3$ above its melting point of 642°C. For the Ca derivative heated at 400°C the broadened X-ray powder diffraction pattern could not be indexed completely with the cubic cell, unlike the Pb derivative. At 700°C, the Ca derivative was transformed into a mixture of Ca$_3$Bi$_2$O$_6$ and an unknown phase; the endothermic peak at 783°C represents the melting point.

The Pb/Bi and Ca/Bi molar ratios in the products were 2.0 as determined by chemical analysis, and the Na contents were negligible (0.1 mass % for both derivatives). Gradual mass losses from room temperature to around 700°C were observed in the TG curves for both compounds. The mass losses in the low temperature region (<300°C) were caused by the removal of adsorbed water molecules, and those in the high temperature region (>300°C) by oxygen evolution during the reduction of Bi$^{5+}$. From these results, the water contents for the Ca and Pb derivatives were calculated to be 1.1 and 1.0, respectively. The water molecules were not incorporated in the crystal structure, but rather were adsorbed on the surface, because the X-ray powder diffraction patterns for the samples heated at 200°C did not change from those of the as-prepared samples. The calculated values of mass loss by the reduction of Bi$^{5+}$ (5.58 and 4.33 mass %) were slightly larger than the observed values (5.08 and 4.09 mass %). The differences suggest that Bi$^{5+}$ in the products

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{X-ray powder diffraction patterns of ABi$_2$O$_6$-type compounds (A: Ca, Sr, Ba, and Pb). Filled circles denote an impurity phase.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{TG-DTA curves of CaBi$_2$O$_6$ and PbBi$_2$O$_6$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{X-ray powder diffraction patterns of CaBi$_2$O$_6$ and PbBi$_2$O$_6$ samples heated at 200–700°C.}
\end{figure}
was partially reduced to Bi$^{3+}$. Consequently, the chemical compositions of the Ca and Pb derivatives were estimated to be CaBi$_2$O$_6$·1.1H$_2$O and PbBi$_2$O$_6$·1.2H$_2$O, respectively, on the basis of the TG mass losses.

### 3.2 Thermodynamic predictions for $\text{ABi}_2\text{O}_6$-type compounds

The formation energies of $\text{A}^2+\text{Bi}_2\text{O}_6$ ($\text{A}^2+$: Mg, Zn, Cd, Ca, Sr, Ba, and Pb) type bismuthates were calculated using the first principle calculations, as shown in Fig. 4. The formation energies of MgBi$_2$O$_6$ and ZnBi$_2$O$_6$ with trirutile-type structures are much lower than those of the PbSb$_2$O$_6$-type one, whereas the formation energies of SrBi$_2$O$_6$ and BaBi$_2$O$_6$ with trirutile-type structures are much higher than those of the PbSb$_2$O$_6$-type structure. From these results, the trirutile-type structure is thermodynamically more favorable in MgBi$_2$O$_6$ and ZnBi$_2$O$_6$, whereas SrBi$_2$O$_6$ and BaBi$_2$O$_6$ prefer to adopt the PbSb$_2$O$_6$-type structure. The actual crystal structures of these bismuthates are consistent with the thermodynamic predictions. On the other hand, in CaBi$_2$O$_6$, CdBi$_2$O$_6$, and PbBi$_2$O$_6$, the differences between the formation energies of the trirutile- and PbSb$_2$O$_6$-type structures are very small, and CdBi$_2$O$_6$ and PbBi$_2$O$_6$ are predicted to adopt trirutile-type structures in contradiction with the actual formation of the PbSb$_2$O$_6$-type structures. CdBi$_2$O$_6$ has a structure related to the PbSb$_2$O$_6$-type with ordering of the Cd and Bi atoms, whereas PbBi$_2$O$_6$ was poorly crystallized. Although CaBi$_2$O$_6$ was predicted to adopt the PbSb$_2$O$_6$-type structure, only a poorly crystallized compound was produced. These structural features for the Ca, Cd, and Pb derivatives may be correlated with the small differences in the formation energies between the trirutile- and PbSb$_2$O$_6$-type structures in the thermodynamic predictions.

### 3.3 Photocatalytic activity of new Ca and Pb bismuthates

Both the Ca and Pb derivatives were photocatalytically active in the decomposition of phenol under visible light irradiation, although the adsorption of phenol was observed under dark conditions, as shown in Fig. 5. NaBiO$_3$ was used as a reference sample because of its high photocatalytic activity for phenol decomposition under visible light irradiation.$^{21}$ All data were obtained under the same experimental conditions. For CaBi$_2$O$_6$·1.1H$_2$O and PbBi$_2$O$_6$·1.2H$_2$O, large amounts of phenol adsorption under dark conditions were observed, while their thermally treated samples and NaBiO$_3$ did not adsorb phenol as strongly in the dark. These differences are considered to be correlated with their poor crystallinity. The slope of the decrease in phenol concentration for the Ca derivative grew steeper upon exposure to visible light, however, the change of the slope for the Pb derivative was small. This result indicates that the photocatalytic activity in the Ca derivative is superior to that for the Pb derivative, and the decrease in phenol concentration for the latter may result predominantly from adsorption rather than decomposition. Nevertheless, photocatalytic activities of the Ca and Pb compounds were lower than that of NaBiO$_3$. The fluorite-type compounds evolved from the Ca and Pb derivatives did not adsorb phenol under dark conditions, and their photocatalytic activities toward phenol decomposition of under visible light were inferior to those of the parent Ca and Pb derivatives.

Figure 6(a) shows the optical absorption spectra of NaBiO$_3$, Ca and Pb derivatives, and their thermally treated samples. The band gap energies were estimated from the dependence of $(\alpha h\nu)^2$ on energy, $h\nu$, (Tauc plot), assuming that direct transitions occur in all bismuthates.$^{21}$ The values of the band gap energies were calculated to be 2.5 (NaBiO$_3$), 2.3 (CaBi$_2$O$_6$·1.1H$_2$O), 2.5 [CaBi$_2$O$_6$ (Flourite-type)], 1.8 (PbBi$_2$O$_6$·1.2H$_2$O), and 1.9 [PbBi$_2$O$_6$ (Flourite-type)] eV, as shown in Fig. 6(b). The high photocatalytic activity of NaBiO$_3$ was explained by its band structure, in which a large dispersion in the conduction band composed of the hybridized Na 3s and O 2p orbitals may suppress the recombination of electron and holes.$^{27}$ The high photocatalytic activity for the Ca derivative may be derived from the comparable band gap value and the similar band structure to NaBiO$_3$. The low photocatalytic activities for the other compounds may be explained by their broad valence bands which is the reason for the low activities toward methylene blue decomposition seen in ZnBi$_2$O$_6$, AgBiO$_3$, and PbBi$_2$O$_6$.$^{21}$

### 4. Conclusions

Two new bismuthates, CaBi$_2$O$_6$·1.1H$_2$O and PbBi$_2$O$_6$·1.2H$_2$O, were prepared from NaBiO$_3$·nH$_2$O. Their X-ray powder diffraction patterns were indexed approximately with the hexagonal cell of the PbBi$_2$O$_6$-type structure. Both CaBi$_2$O$_6$·1.1H$_2$O and PbBi$_2$O$_6$·1.2H$_2$O exhibited photocatalytic activity in the decom-
position of phenol under visible light irradiation, and the activity of the former compound was superior.

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