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Photocatalytic activities of various pentavalent bismuthates under visible light irradiation

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ABSTRACT

$LiBiO_3$, $NaBiO_3$, $MgBi_2O_6$, $KBiO_3$, $ZnBi_2O_6$, $SrBi_2O_6$, $AgBiO_3$, $BaBi_2O_6$ and $PbBi_2O_6$ were synthesized by various processes such as hydrothermal treatment, heating and so on. These materials were examined for their photocatalytic activities in the decolorization of methylene blue and decomposition of phenol under visible light irradiation. For methylene blue decolorization, the presence of $KBiO_3$ resulted in complete decoloration within 5 min. For phenol decomposition, $NaBiO_3$ showed the highest activity, while $LiBiO_3$, $SrBi_2O_6$ and $BaBi_2O_6$ possessed almost comparable decomposition rates. Their decomposition rates were apparently higher than that by anatase (P25) under UV irradiation.

1. Introduction

Various oxides have been examined for photocatalytic activities to decompose organic species or H_2O by many researchers. The performance of the photocatalysts was determined by many factors such as shape of devices, density of states, wavelength of irradiated light and so on. The electronic structure is especially important for photocatalytic activity. For most oxides, the potential of the top of the valence band composed of O 2*p* is at around 3 eV, and the bottom of the conduction band composed of metal orbitals determines the band gap energy. For instance, the band gap energy of anatase single crystals is around 3.2 eV, which is composed of O 2*p* at approximately 3 eV in the valence band and Ti 3*d* at approx. −0.2 eV in the conduction band. Thus, anatase can absorb UV light at around 390 nm or shorter wavelengths. Generally, in order to improve visible light responsiveness, substitution of carbon [1], nitrogen [2–6] or sulphur [4,7] for oxygen in the metal oxide has been reported to result an upward shift of the valence band so decreasing the band gap.

The other method for control of the band gap is substitution of metal in the oxides. Metal bismuthates are strong candidates for photocatalytic materials for decomposition of organic species. For example, trivalent bismuthates, $BiVO_4$, $CaBi_2O_4$, Bi_2WO_6 and so on have a yellow color because Bi 6*s* and O 2*p* hybrid orbital is broad and resultant band gap becomes narrow [8–14]. Therefore, visible light can excite the electrons and positive empty holes can oxidize some organic species. The Bi^{3+} cation has two 6*s* electrons and a d^{10} closed shell. On the other hand, Bi^{5+} has an empty 6*s* orbital but still has a d^{10} closed shell. Therefore, pentavalent bismuthates must have different electronic structure compared with trivalent bismuthates. Kako et al. [15] have reported that $NaBiO_3$ has efficient photocatalytic activities for methylene blue decomposition. $NaBiO_3$ has the ilmenite structure, which is composed of pentavalent bismuth, oxygen and a sodium cation. Many pentavalent bismuthates were reported in terms of their synthesis and crystal structure. Other pentavalent bismuthates should be examined for electronic structure and photocatalytic activity. In this study, nine pentavalent bismuthates, $LiBiO_3$, $NaBiO_3$, $MgBi_2O_6$, $KBiO_3$, $ZnBi_2O_6$, $SrBi_2O_6$, $AgBiO_3$, $BaBi_2O_6$ and $PbBi_2O_6$ were prepared and were examined for photocatalytic activity.

2. Material and methods

2.1. Preparation of pentavalent bismuthates

The nine pentavalent bismuthates were prepared as follows. At first we prepare $NaBiO_3$ by dehydration of $NaBiO_3 \cdot nH_2O$ [16]. $AgBiO_3$ almost has the same structure as $NaBiO_3$, which is prepared by the hydrothermal process from $NaBiO_3 \cdot nH_2O$ in $AgNO_3$ aqueous

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solution at 70 °C [17]. These compounds have ilmenite structure. The pentavalent bismuthates with a different structure which is the same as lead antimonate is obtained by hydrothermal treatment at 90–130 °C for approximately 1 week from $NaBiO_3 \cdot nH_2O$ in Sr or Ba chloride aqueous solution. The chemical formulae of the obtained compounds are $SrBi_2O_6$ and $BaBi_2O_6$, respectively. $PbBi_2O_6$ with the same structure was prepared by simply stirring $NaBiO_3 \cdot nH_2O$ in $Pb(NO_3)_2$ aqueous solution. The trirutile-type structure was observed for $MgBi_2O_6$ and $ZnBi_2O_6$, which were prepared by hydrothermal treatment of $NaBiO_3 \cdot nH_2O$ with $MgCl_2$ or $Zn(NO_3)_2$ aqueous solutions at 130 and 90 °C, respectively [18]. $LiBiO_3$ was prepared by the stirring process in LiCl aqueous solution [19]. $KBiO_3$ was prepared from $NaBiO_3 \cdot nH_2O$ by heating with KOH at 250 °C.

2.2. Characterization

The resultant samples were identified by X-ray diffraction (XRD) (RINT-2000, Rigaku) and their surface areas were measured by N_2 gas adsorption (BELSORP-mini, Nippon BEL). The point of zero charge (pzc) was measured by ζ potential measurement (Zetasizer Nano-Z, Malvern Instruments, Ltd.). The photocatalytic activities were examined for decomposition of methylene blue as a screening examination and that of phenol under visible light with a cut-off at 420 nm. The experiments on the decomposition of methylene blue were carried out as follows. Methylene blue aqueous solution at a concentration of 16 ppm was prepared by using distilled water, and the sample bismuthate was put into the methylene blue solution at a concentration of 3 g/L. The solution was stirred and was irradiated by visible light from a 300 W Xe lamp (UXR-300DU, Ushio Inc.) with 420 nm sharp cut filter (GG420, SHIBUYA OPTICAL Co., Ltd.). A couple of milliliters were extracted from the solution at 10, 20, 40, 60, 80, 100 and 120 min of elapsed time. For investigation of adsorption effect, the same measurements were carried out under dark condition (no irradiation of visible light). The concentration of methylene blue in the solution was measured from the optical absorbance at 651 nm by UV–vis spectroscopy (V-550, JASCO).

Phenol decomposition was examined under visible light as follows. TOC (total organic carbon) in the solution was measured by total organic carbon analyzer (TOC-V_{CSH}, Shimadzu) and phenol concentration by LC (liquid chromatography) (Prominence

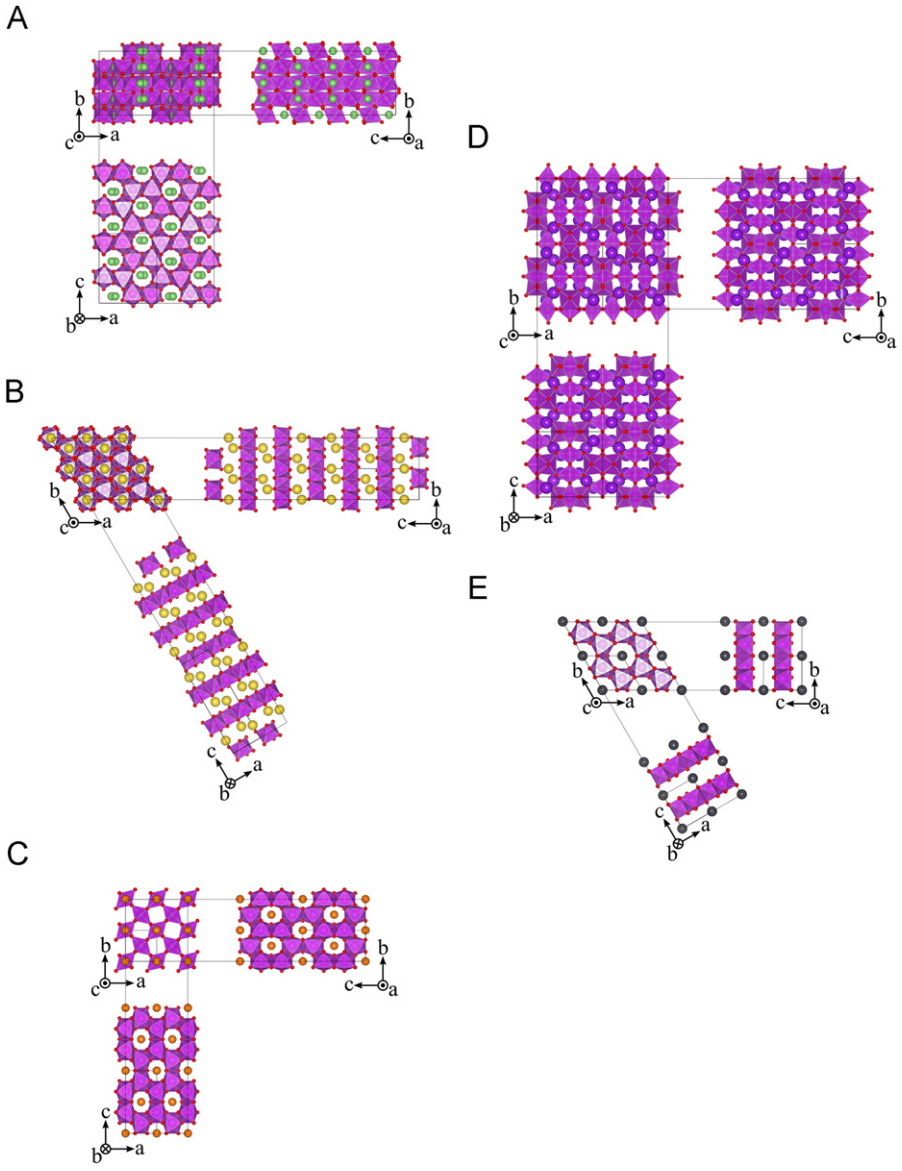

Fig. 1. Crystal structures of the pentavalent bismuthates used in this paper: (A) $LiBiO_3$, (B) $NaBiO_3$ and $AgBiO_3$, (C) $MgBi_2O_6$ and $ZnBi_2O_6$, (D) $KBiO_3$ and (E) $SrBi_2O_6$, $BaBi_2O_6$ and $PbBi_2O_6$.