



Photocatalytic activities of various pentavalent bismuthates under visible light irradiation

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ABSTRACT

LiBiO₃, NaBiO₃, MgBi₂O₆, KBiO₃, ZnBi₂O₆, SrBi₂O₆, AgBiO₃, BaBi₂O₆ and PbBi₂O₆ 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 KBiO₃ resulted in complete decoloration within 5 min. For phenol decomposition, NaBiO₃ showed the highest activity, while LiBiO₃, SrBi₂O₆ and BaBi₂O₆ possessed almost comparable decomposition rates. Their decomposition rates were apparently higher than that by anatase (P25) under UV irradiation.

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1. Introduction

Various oxides have been examined for photocatalytic activities to decompose organic species or H₂O 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, BiVO₄, CaBi₂O₄, Bi₂WO₆ 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 Bi³⁺ cation has two 6*s* electrons and a *d*¹⁰ closed shell. On the other hand, Bi⁵⁺ 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 NaBiO₃ has efficient photocatalytic activities for methylene blue decomposition. NaBiO₃ 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, LiBiO₃, NaBiO₃, MgBi₂O₆, KBiO₃, ZnBi₂O₆, SrBi₂O₆, AgBiO₃, BaBi₂O₆ and PbBi₂O₆ 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 NaBiO₃ by dehydration of NaBiO₃ · *n*H₂O [16]. AgBiO₃ almost has the same structure as NaBiO₃, which is prepared by the hydrothermal process from NaBiO₃ · *n*H₂O in AgNO₃ 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 $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$ 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 $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$ in $\text{Pb}(\text{NO}_3)_2$ aqueous solution. The trirutile-type structure was observed for MgBi_2O_6 and ZnBi_2O_6 , which were prepared by hydrothermal treatment of $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$ with MgCl_2 or $\text{Zn}(\text{NO}_3)_2$ 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 $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$ 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

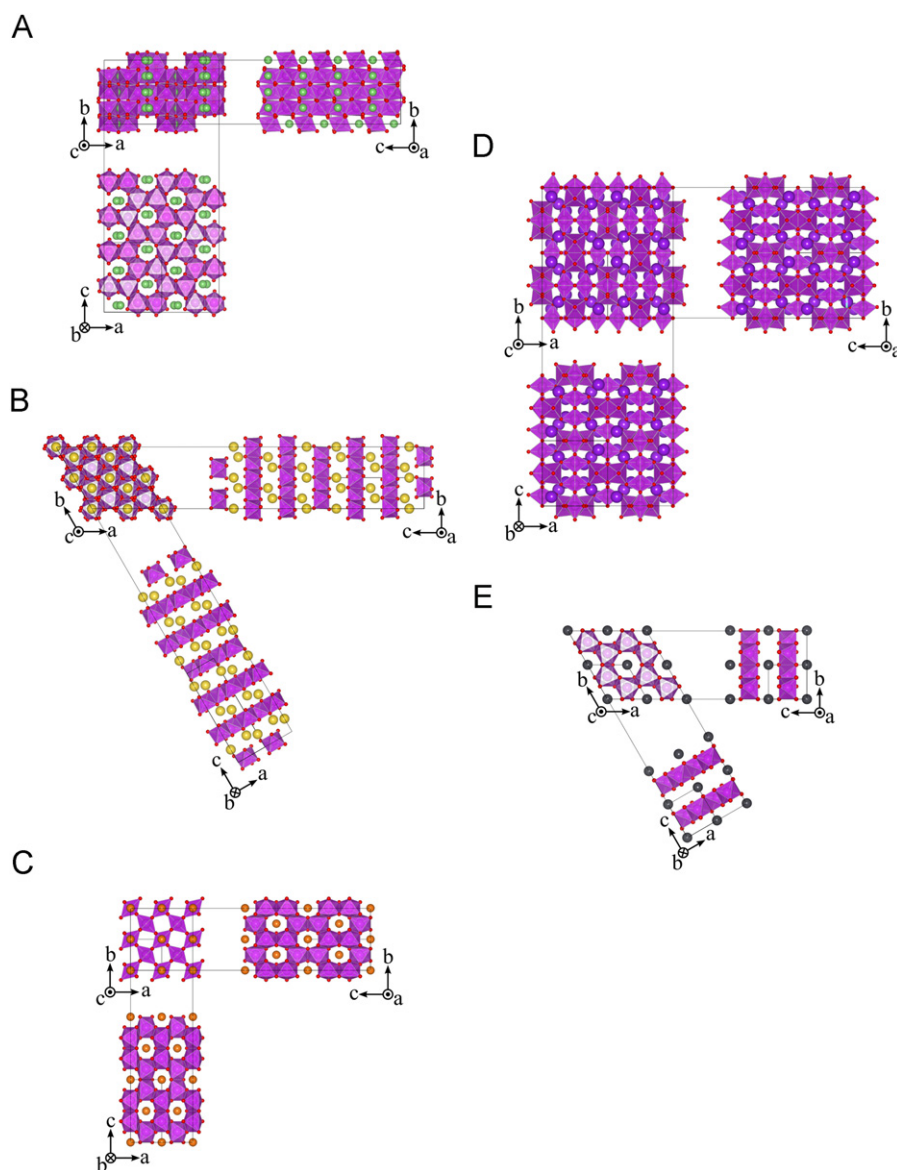


Fig. 1. Crystal structures of the pentavalent bismuthates used in this paper: (A) LiBiO_3 , (B) NaBiO_3 and AgBiO_3 , (C) MgBi_2O_6 and ZnBi_2O_6 , (D) KBiO_3 and (E) SrBi_2O_6 , BaBi_2O_6 and PbBi_2O_6 .

LC-20AT, Shimadzu). For the first 60 min, the solution was stirred without irradiation of the visible light in order to examine adsorption of phenol. After 60 min, visible light was irradiated.

Fig. 1 shows the crystal structures ($2 \times 2 \times 2$ of the unit cell) of the pentavalent bismuthates used in this paper. Projection views are shown [001], [100] and $[0\bar{1}0]$ directions located at upper left, upper right and lower left, respectively. All octahedra or distorted octahedra are BiO_6 in these figures. The spheres indicate other cations. The crystal structures of the pentavalent bismuthates used in this paper are divided into 5 groups, (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 . These space groups are $Pccn$, $R\bar{3}$, $P4_2/mnm$, $Pn\bar{3}$ and $P\bar{3}1m$, respectively. NaBiO_3 and AgBiO_3 in (B) show the ilmenite structure. MgBi_2O_6 and ZnBi_2O_6 apparently have trirutile structure. KBiO_3 (D) shows another type of crystal structure in which edge-shared two distorted BiO_6 octahedral form one unit which connects four units by corner sharing. SrBi_2O_6 , BaBi_2O_6 and PbBi_2O_6 have a same structure as PbSb_2O_6 as shown in (E). The electronic band structure calculations of these bismuthates were carried out by DV- $X\alpha$ (discrete-variational $X\alpha$ molecular orbital method) method using a program "SCAT" [20] from these crystal structures. The clusters composed of 10 bismuth atoms and several other cations were build. The DOS (density of state) was calculated using the electron orbitals of O, Bi^{5+} , and the other cations. The cluster was embedded

in the Madelung potential field which was made from each crystal structure.

3. Results and discussion

3.1. Decomposition of methylene blue

The specific surface areas of the synthesized pentavalent bismuthates were measured by N_2 adsorption, and were 8.9, 5.4, 7.6, 1.9, 12.3, 5.7, 5.4 and $2.9 \text{ m}^2/\text{g}$ for LiBiO_3 , NaBiO_3 , KBiO_3 , MgBi_2O_6 , SrBi_2O_6 , BaBi_2O_6 , ZnBi_2O_6 and AgBiO_3 , respectively. These surface areas are relatively small.

Fig. 2(a) and (b) shows the relationships between elapsed time and concentration of methylene blue under visible light irradiation. Fig. 3(a) and (b) shows those under dark circumstance. From these plots, the concentration of the methylene blue for the solution of blank (without sample) did not show significant decrease within 40 min in this experiment. For NaBiO_3 , the reproducibility was confirmed under the visible light irradiation. Since the average error was within several percent, these experiments seem to be reasonable reproducibility. For ZnBi_2O_6 and PbBi_2O_6 , the concentration of methylene blue seems not to be decreased under dark and visible light irradiation. For MgBi_2O_6 ,

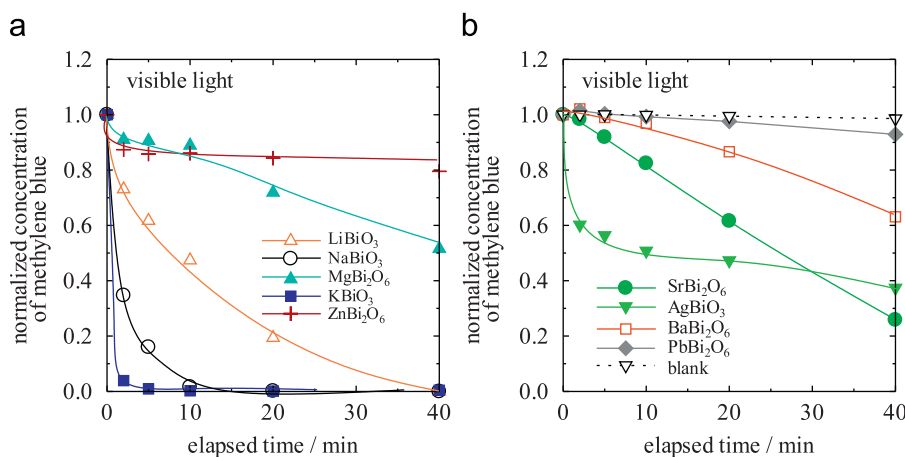


Fig. 2. Dependence of the normalized concentration of methylene blue in the presence of pentavalent bismuthates as a function of time under visible light irradiation: (a) LiBiO_3 , NaBiO_3 , MgBi_2O_6 , KBiO_3 and ZnBi_2O_6 and (b) SrBi_2O_6 , AgBiO_3 , BaBi_2O_6 and PbBi_2O_6 .

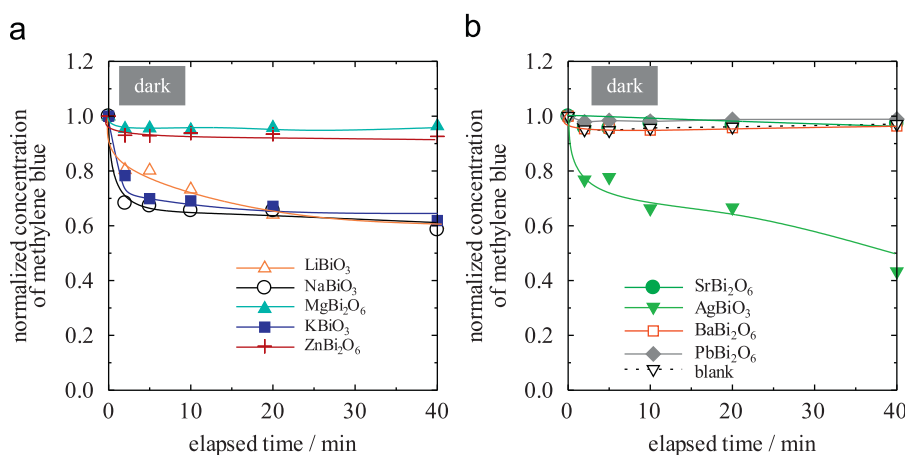


Fig. 3. Dependence of the normalized concentration of methylene blue in the presence of pentavalent bismuthate with pentavalent Bi as a function of time under dark circumstance: (a) LiBiO_3 , NaBiO_3 , MgBi_2O_6 , KBiO_3 and ZnBi_2O_6 and (b) SrBi_2O_6 , AgBiO_3 , BaBi_2O_6 and PbBi_2O_6 .

SrBi₂O₆, and BaBi₂O₆, the methylene blue concentration decreased linearly and 30–70% of the methylene blue decomposed. In the absence of irradiation, the concentration did not decrease. For AgBiO₃, the concentration decrease by around 50–60% under both irradiation of visible light and in the dark. The plot confirms that only adsorption of methylene blue occurs on the AgBiO₃. For LiBiO₃, NaBiO₃ and KBiO₃, methylene blue was completely decomposed within 40 min of irradiation. Especially for KBiO₃, the rate of decrease seems to be much higher than the others. After minutes, KBiO₃ already decolorized 95% of the methylene blue. For dark condition, the concentration decreases by around 40%. Such decrease apparently results from adsorption. That is, both photocatalytic decomposition and adsorption of methylene blue occurred in these samples. From these results, alkali or alkaline earth bismuthates(V) have apparently higher photocatalytic ability for decoloration of methylene blue. For alkali bismuthates, both photocatalytic decomposition and adsorption occurs, while only photocatalytic decomposition occur for alkaline earth bismuthates.

The adsorption of methylene blue occurred on LiBiO₃, NaBiO₃, KBiO₃ and AgBiO₃, whereas the adsorption did not observe on MgBi₂O₆, ZnBi₂O₆, SrBi₂O₆, BaBi₂O₆ and PbBi₂O₆. We measured the point of zero charge (pzc) of NaBiO₃, KBiO₃, MgBi₂O₆ and SrBi₂O₆. The values of pzc are almost similar of around 2–3. The aqueous solution of methylene blue is around 6–7, and the methylene blue is cationic in the aqueous solution. Therefore, an attractive force between all bismuthate particles and methylene blue cations may emerge. However, the methylene blue cation tends to adsorb on only LiBiO₃, NaBiO₃, KBiO₃ and AgBiO₃. This result indicates that the methylene blue adsorption occurs by a kind of chemisorption rather than by the electrostatic attractive force. In fact, the bismuthates on which the methylene blue adsorbed are composed of monovalent cation, pentavalent bismuth and oxygen (M^+BiO_3). The other bismuthates are composed of divalent cation, pentavalent bismuth and oxygen ($M^{2+}Bi_2O_6$).

The number of bismuth atom of M^+BiO_3 is smaller than those of $M^{2+}Bi_2O_6$. These considerations plausibly mean that the methylene blue might not adsorb on the compound with large amount of bismuth.

Fig. 4(a) and (b) shows the UV–vis spectra of these samples. Most of the samples show absorbance of visible light with relatively short wavelength. Absorption edges seemed to be distributed between approximately 500 and 800 nm. NaBiO₃ shows the shortest wavelength of the absorption edge. For AgBiO₃, the color is black and high absorbance observed throughout all wavelengths. Band gap energies of all bismuthates were estimated from the dependence of $(\alpha h\nu)^2$ on energy, $h\nu$, assuming that direct transition occurs in all bismuthates. The estimated band gap energies and colors are shown in Table 1. The sample colors are probably agreeable with band gap energies. By comparison of photocatalytic decomposition activity and UV–vis spectra, a general trend with some exceptions is apparent in that higher decomposition rates are associated with lower wavelength absorption edges. From these results, alkali or alkaline earth bismuthates(V) are determined by screening to use phenol decomposition.

3.2. Decomposition of phenol

Fig. 5 shows the dependence of TOC on elapsed time for phenol decomposition under visible light (cut by 420 nm cut-off filter) with LiBiO₃, NaBiO₃, KBiO₃, SrBi₂O₆ and BaBi₂O₆, and under UV–vis light (without 420 nm cut-off filter) with TiO₂(P25). For the initial 60 min, the experiment was carried out in dark conditions (without irradiation) to examine the extent of adsorption of phenol on the samples. For all samples, since the concentration seemed to be invariant, phenol molecules were found to be not adsorbed on the samples. Since the phenol is very weak acid, negatively charged phenol cannot adsorb on the bismuthates because the pzc of them is 2–3. After completion of

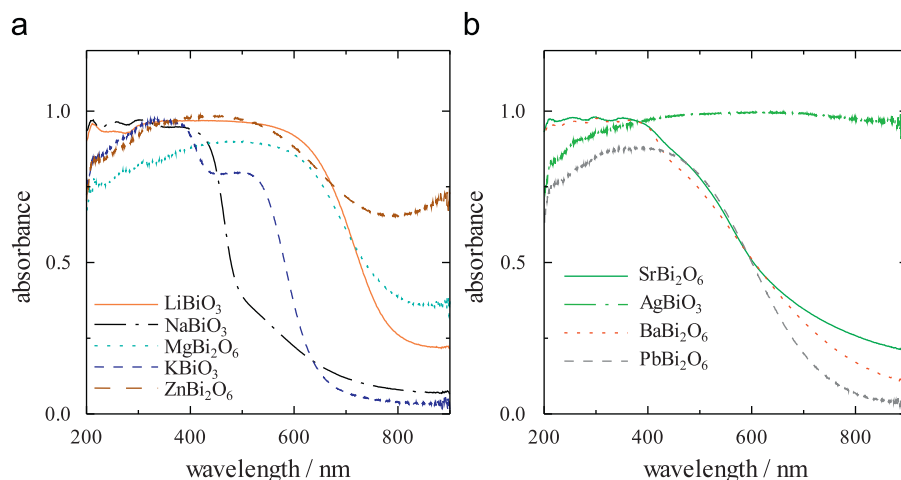


Fig. 4. UV–vis spectra of the prepared pentavalent bismuthates: (a) LiBiO₃, NaBiO₃, MgBi₂O₆, KBiO₃ and ZnBi₂O₆ and (b) SrBi₂O₆, AgBiO₃, BaBi₂O₆ and PbBi₂O₆.

Table 1
Estimated band gap energies (eV) from UV–vis spectra and sample color.

Sample	LiBiO ₃	NaBiO ₃	KBiO ₃	MgBi ₂ O ₆	SrBi ₂ O ₆	BaBi ₂ O ₆	ZnBi ₂ O ₆	AgBiO ₃	PbBi ₂ O ₆
Band gap (eV)	1.63	2.53	2.04	1.61	1.93	1.93	1.53	0.87	1.92
Color	Ye	Ye	Re	Br	Br	Br	Br	Bl	Br

Ye: yellow, Re: red, Br: brown, Bl: black.

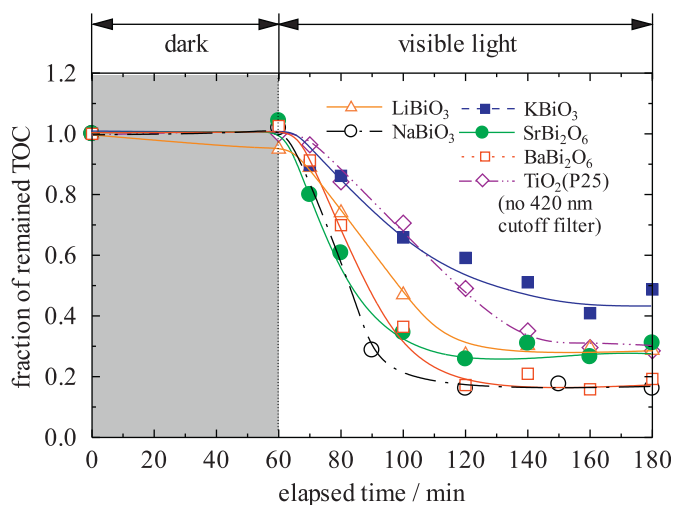


Fig. 5. Dependence of TOC changes in the presence of the pentavalent bismuthates as a function of time under dark (up to 60 min) and visible light irradiation (after 60 min).

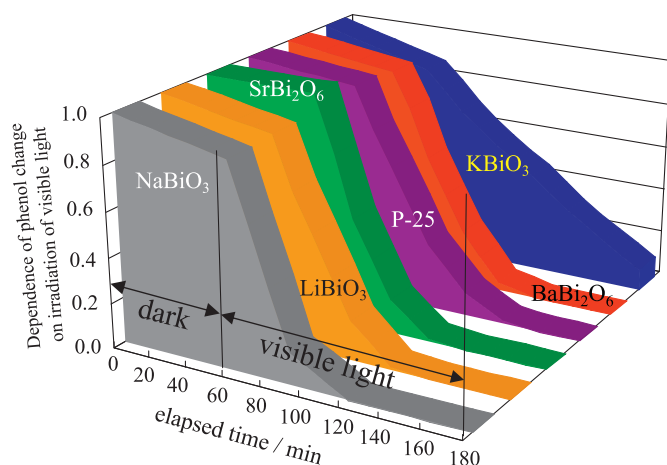


Fig. 6. Dependence of phenol change in the presence of the pentavalent bismuthates as a function of time under visible light irradiation.

the irradiation, the solution increased in temperature by ten or several tens of degree centigrade. The effect of increase in temperature is no large for photocatalytic reaction because band gap is enough large compared to the increase in temperature. For the irradiation period of visible light, the TiO₂ apparently decomposed phenol linearly and the concentration seemed to be constant at longer than around 100 min under UV-vis light (160 min by elapsed time). For almost all the bismuthates irradiated by only visible light, phenol concentration decreased faster than that of TiO₂ (with UV-vis light irradiation) and converged to around 20–40% of initial concentration. The decomposition rate by NaBiO₃ is the fastest of all samples; however, SrBi₂O₆ and BaBi₂O₆ decomposed phenol comparably quickly. On the other hand, phenol decomposed relatively slowly (slower than that of TiO₂) with KBiO₃. This result seems to be incompatible with that for decomposition of methylene blue. In fact, methylene blue can decolorize by three processes; oxidation by holes and superoxide anions, and reduction by excited electrons. The decomposition of organic molecules is usually occurs via oxidation by holes. For methylene blue, the molecule is reduced by electrons at a relatively low potential of approximately -0.07 to -0.08 V vs SHE [21]. The protons in the solution are reduced to generate H₂ at 0 V, and O₂ can be more easily reduced to form superoxide

anion. On the other hand, H₂O and Cl⁻ can be oxidized at 1.23 and 1.36 V, respectively. Thus, photo-excited electron can decolorize methylene blue if the bottom of the conduction band is higher than the potential for formation of leucomethylene blue. For KBiO₃, both decoloration and decomposition might occur because the phenol decomposition occurs gradually despite the rapid decoloration of the methylene blue.

The phenol concentrations converge on approx. 20–40% of the initial concentration, as mentioned before. The remainder of TOC was examined by LC. Fig. 6 shows the amount of phenol in the solution measured by LC. For NaBiO₃, LiBiO₃ and SrBi₂O₆, the amount of phenol decreased till 1 h and then the decomposition completed. For TiO₂ (with UV-vis irradiation) and BaBi₂O₆, the decomposition rate seems to be relatively slow. Thus, these samples possibly decompose phenol completely and some segments which can be regarded as organic hydrocarbon formed. For KBiO₃, the amount reached at around 0.1 by the irradiation for 120 min (elapsed time for 180 min). This result showed that KBiO₃ has lower activity for decompose phenol comparing to the other samples.

3.3. DOS consideration

Fig. 7(a) and (b) shows the DOS curves composed of each orbitals from O, Bi⁵⁺ and the other cations. In these curves, the top of the valence band is fixed at 0 eV. General trend is larger simulated band gap than the gap measured via UV-vis spectrum. In most of the compounds, conduction and valence band are derived from O 2p and Bi 6s orbitals, respectively. For NaBiO₃ and AgBiO₃, they have same ilmenite structure though very different DOS curves. For the NaBiO₃, the calculated band gap is around 4.3 eV. For the AgBiO₃ plot, the broad Ag 4d orbital is above the O 2p by around 2–3 eV. This Ag 4d orbital seems to fill band gap. This orbital may contribute electronic conductivity of the AgBiO₃. In fact, the color of AgBiO₃ is black as mentioned in Table 1. Actually, AgBiO₃ is an electrical conductor.

For the pentavalent bismuthate with the lead antimonate structure, SrBi₂O₆, BaBi₂O₆, and PbBi₂O₆, DOS curves of PbBi₂O₆ seem to be apparently different. Pb 6s appeared at around -2 eV and it results in a decrease of the band gap. SrBi₂O₆ and BaBi₂O₆ have a slightly narrow band gap compared to the NaBiO₃. For these compounds, the DOS curves are in the same manner. Both materials are composed of alkaline earth cation and pentavalent bismuth, and they have same structure. The similar DOS and photocatalytic properties seem to be reasonable. For MgBi₂O₆ and ZnBi₂O₆ which have the trirutile structure, band gap of ZnBi₂O₆ is slightly narrower than that of MgBi₂O₆ due to broad valence band in ZnBi₂O₆. The photonic band gap in Table 1 shows same trend. The broad valence band in ZnBi₂O₆ is composed of O 2p and Zn 3d orbitals.

For LiBiO₃, the DOS curve resembles that of the NaBiO₃. Alkali cations generally form ionic bonds, hybrid orbital do not emerge and then the alkali seems not to affect electronic structure of the materials. On the other hand, for KBiO₃, the crystal structure is unique in this paper. In the DOS curve, O 2p splits consequently the band gap becomes narrow. Actually, the sample color is red as shown in Table 1. In this structure, two type oxygen atoms exist as follows; edge-shared and corner-shared oxygen. Therefore, BiO₆ octahedra are prone to distort. In the DV-X α simulation, the edge-shared oxygen shows relatively higher energy than corner-shared oxygen in this material. In addition, bottom of the conduction band is relatively low because of a new level which is composed of Bi 6s and O 2p emerged at around 2.2 eV. This low level may relate to the decoloration of methylene blue as mentioned above.

The low activity for methylene blue decomposition for ZnBi₂O₆, AgBiO₃ and PbBi₂O₆ probably result from the broad valence bands. That is, the valence band in these bismuthates is composed of O 2p and d electron. On the other hand, a relatively slow decomposition

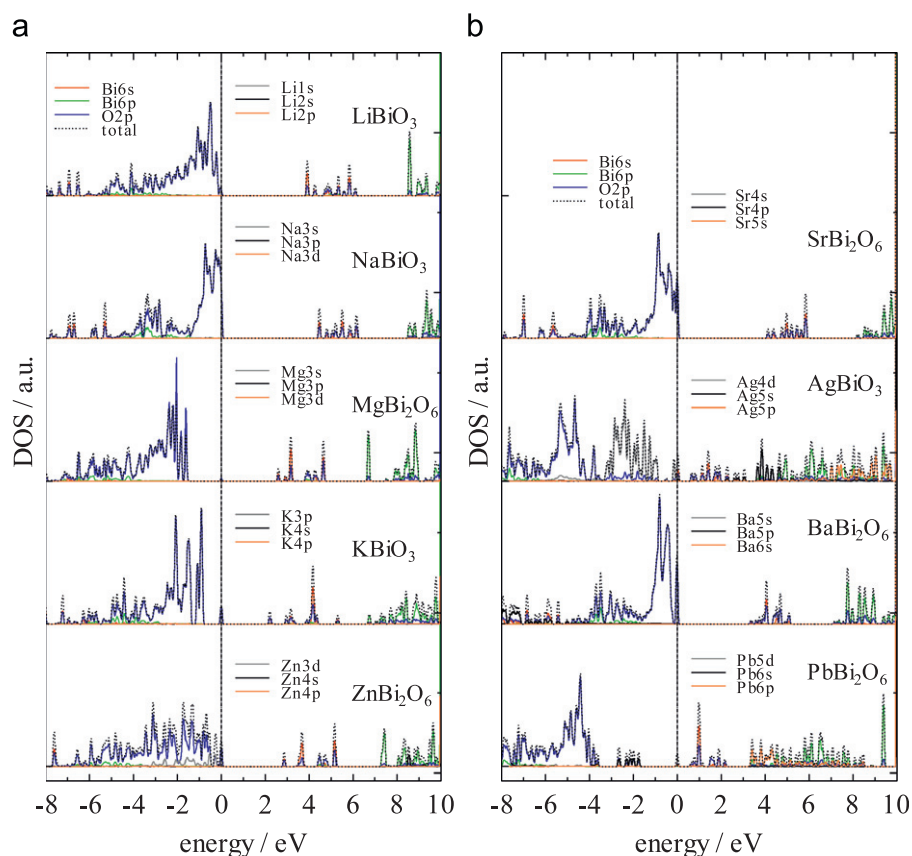


Fig. 7. DOS curves of the pentavalent bismuthates calculated by DV- $X\alpha$: (a) LiBiO_3 , NaBiO_3 , MgBi_2O_6 , KBiO_3 and ZnBi_2O_6 and (b) SrBi_2O_6 , AgBiO_3 , BaBi_2O_6 and PbBi_2O_6 .

rate of phenol by KBiO_3 is possibly due to the split of O 2p. The band gap of KBiO_3 is narrow because of the split of O 2p and upshift the valence band. Such upshift generally decrease oxidation activity.

4. Conclusions

In conclusion, alkali and alkaline earth pentavalent bismuthates, LiBiO_3 , NaBiO_3 , SrBi_2O_6 and BaBi_2O_6 possess high photocatalytic activity under visible light. The decomposition of phenol by them under visible light is faster than that by anatase (P25) under UV–vis light. Therefore, these seem to be strong candidates for visible light-sensitive photocatalysts for decomposition of organic species. The activities for decomposition of organic species seem to be strongly affected by the electronic structure of the samples. Especially, the *d* electron of Zn, Ag and Pb possibly contribute to form a broad conduction band and the photocatalytic activities for decomposition of organic molecules consequently are prone to be diminished.

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