Photophysical and Photocatalytic Properties of Molybdates and Tungstates with a Scheelite Structure

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Photophysical and photocatalytic properties of molybdates and tungstates with a scheelite structure were investigated. The band gaps of scheelite compounds narrowed when the compounds were composed of Ag^+ and Bi^{3+} ions. $(NaBi)_{0.5}MoO_4$ (BG: 3.1 eV) and $(AgBi)_{0.5}MoO_4$ (BG: 3.0 eV) showed the photocatalytic activities for O_2 evolution from an aqueous solution containing an electron acceptor. On the other hand, $(NaBi)_{0.5}WO_4$ (BG: 3.5 eV) produced H_2 from an aqueous solution containing an electron donor.

Photocatalytic water splitting is an attractive reaction from the viewpoint of photon energy conversion. It has been reported that some metal oxides function as highly active photocatalysts for water splitting.[1–6] Development of highly efficient photocatalysts with a visible light response is desired in terms of utilization of solar energy. However, the satisfying photocatalyst has not been found at the present stage. Therefore, the research to survey new photocatalyst materials is still important. The photocatalysts for water splitting are mainly oxide materials based on Ti,[1,2,7] Nb,[1,2] Ta,[2–4,8–11] Ga,[5] and In.[6] It has been reported that, for compounds consisting of the sixth group element, some polytungstates are homogeneous photocatalysts for H_2 evolution from an aqueous solution containing an electron donor.[12] On the other hand, there are only a few reports about W-based heterogeneous photocatalysts, $Na_2W_4O_{13}$,[13] $Bi_2W_2O_9$,[14] and Bi_2WO_6,[14] besides WO_3.[15] These W-based photocatalysts can produce not only O_2 but also H_2 from an aqueous solution containing sacrificial reagents. This result suggests the possibility that some W-based photocatalysts with the activity for water splitting may be developed.

There are many reports for perovskite-related photocatalysts.[1–4,7–11,14] Therefore, the perovskite-related structure seems to be advantageous for photocatalysts. On the other hand, $BiVO_4$ which is a highly efficient photocatalyst for O_2 evolution under visible light irradiation has a monoclinic scheelite structure.[16] $PbMoO_4$ is also a scheelite-type photocatalyst.[17] The scheelite structure is also interesting as a crystal structure of a photocatalyst. In the present study, photophysical and photocatalytic properties of molybdates and tungstates with the scheelite structure are investigated. The effects of component ions, especially Ag^+ and Bi^{3+}, on the photophysical properties are also discussed.

The powders of molybdates and tungstates were obtained by solid-state syntheses. Oxides and carbonates of the starting materials were mixed in a stoichiometric ratio. The mixture was calcined at 803–1123 K for 5 h in air using an alumina crucible. The obtained powders were confirmed by X-ray diffraction (Rigaku; MiniFlex). A platinum cocatalyst was loaded from an aqueous H_2PtCl_6 solution by a photodeposition method. Photocatalytic H_2 or O_2 evolution from water containing sacrificial reagents was carried out in a gas-closed circulation system as reported in the previous literature.[11] The light source was a 300-W Xe-arc lamp (Parkin-Elmer; Cermax-LX300F). The evolved H_2 and O_2 were analyzed by gas chromatography. Diffuse reflection spectra of molybdates and tungstates were measured using a UV–vis-NIR spectrometer (Jasco; Ubest-V570) and were converted from reflectance to absorbance by the Kubelka–Munk method. Photoluminescence was measured at 77 K using a fluorescence spectrometer (Spex; FluoroMax).

XRD patterns of $(A1A2)_{0.5}MoO_4$ (A1: Na^+, Ag^+, A2: Ln^{3+}, Bi^{3+}) were assigned to a tetragonal scheelite structure. The diffraction peaks shifted appropriately according to the ion sizes of A1 and A2 cations. $(NaBi)_{0.5}WO_4$ also possessed a scheelite structure. The diffraction pattern of $(AgBi)_{0.5}WO_4$ was different from that of scheelite although there was a report in JCPDS (37-102) that $(AgBi)_{0.5}WO_4$ had a $CaWO_4$ type structure.

The positions of absorption bands of the scheelite-type compounds were changed with the component ions as shown in Figure 1. Band gaps estimated from the onsets of the absorption are listed in Table 1. Among the molybdates, $(NaLa)_{0.5}MoO_4$ had the widest band gap (3.9 eV) which was the same value as the band gap of $CaMoO_4$. The band gaps of $(AgLa)_{0.5}MoO_4$ and $(NaBi)_{0.5}MoO_4$ were narrower by 0.4 and 0.8 eV than that of $(NaLa)_{0.5}MoO_4$, respectively. Moreover, $(AgBi)_{0.5}MoO_4$ had a narrower band gap than $(AgLa)_{0.5}MoO_4$ and $(NaBi)_{0.5}MoO_4$. This result indicates that the valence band of $(AgBi)_{0.5}MoO_4$ would be formed at a more negative position by the synergetic effect of Ag^+ and Bi^{3+} than that consisting of Ag^+ or Bi^{3+}. $(AgCe)_{0.5}MoO_4$ showed the intense absorption in the visible light region. Its band gap was estimated to be 2.3 eV from the
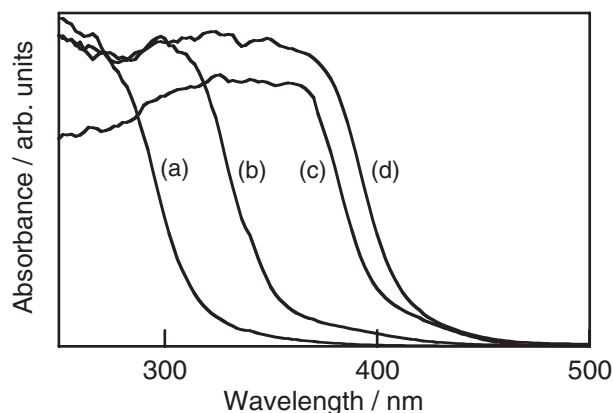

Figure 1. Diffuse reflection spectra of scheelite-type molybdates at room temperature, (a) $(NaLa)_{0.5}MoO_4$, (b) $(AgLa)_{0.5}MoO_4$, (c) $(NaBi)_{0.5}MoO_4$, and (d) $(AgBi)_{0.5}MoO_4$.

Table 1. Photocatalytic activities of scheelite-type molybdates and tungstates

Catalyst	BG /eV	Activity/μmol h^{-1}	
		H$_2$[a]	O$_2$[b]
(NaLa)$_{0.5}$MoO$_4$	3.9	—	—
(NaBi)$_{0.5}$MoO$_4$	3.1	0.6	58
(AgLa)$_{0.5}$MoO$_4$	3.5	0	1.1
(AgBi)$_{0.5}$MoO$_4$	3.0	0	10.7
(AgCe)$_{0.5}$MoO$_4$	2.3	0	0
(AgEu)$_{0.5}$MoO$_4$	3.2	0	1.1
(AgYb)$_{0.5}$MoO$_4$	3.1	0	0
(NaBi)$_{0.5}$WO$_4$	3.5	7.0	1.3
(AgBi)$_{0.5}$WO$_4$	3.2	0.1	5.8

[a]From an aq. CH$_3$OH solution (10 vol %), Pt (0.5 wt %) cocatalyst loaded, [b]from an aq. AgNO$_3$ solution (0.05 mol L^{-1}). Catalyst: 0.3 g, reactant solution: 150 mL, light source: 300-W Xe lamp, cell: top-irradiation cell with Pyrex a window.

onset of absorption. The narrow band gap of (AgCe)$_{0.5}$MoO$_4$ seemed to be due to the contribution of the Ce4f orbital to formation of the valence band.[18] On the other hand, when La^{3+} ions in (AgLa)$_{0.5}$MoO$_4$ were replaced with Eu^{3+} and Yb^{3+} which can take a divalent oxidation number, the band gaps were narrowed. For the tungstates, the replacement of Ca^{2+} ions in CaWO$_4$ (BG: 4.4 eV) with Na$^+$ and Bi^{3+} ions made the band gap narrower by 0.9 eV as the case of molybdates. Moreover, the synergetic effect of Ag$^+$ and Bi^{3+} on the narrowing the band gap was also observed for (AgBi)$_{0.5}$WO$_4$ although its structure was not a scheelite-type. These results conclude that Ag4d and Bi6s orbitals form the valence bands of scheelite-type compounds more negatively than that consisting of the only O2p orbitals observed for AgNbO$_3$[11] and BiVO$_4$.[16] The excited energy is generally localized in isolated MoO$_4$ tetrahedra in a scheelite structure. The excited energy may be delocalized more or less when Ag4d and Bi6s contribute to the band formation. The delocalization of the excited energy would also affect the narrowing the band gap.

Photoluminescence of molybdates was investigated to confirm the change in the energy structure. (NaLa)$_{0.5}$MoO$_4$, (AgLa)$_{0.5}$MoO$_4$, and (NaBi)$_{0.5}$MoO$_4$ showed broad emission bands with maxima at 560 nm by the band gap excitation at 77 K. The onsets of excitation spectra agreed with those of absorption spectra. Thus, it was revealed that the replacement of Na$^+$ and La^{3+} ions with Ag$^+$ and Bi^{3+} ions made the excitation bands for luminescence of MoO$_4{}^{2-}$ shift to the red side. On the other hand, (AgEu)$_{0.5}$MoO$_4$ showed sharp emission at 614 nm assigned to the emission from Eu^{3+} ions by excitation of not only Eu^{3+} ions but also the band gap. In contrast, no emission was observed for (AgCe)$_{0.5}$MoO$_4$, (AgYb)$_{0.5}$MoO$_4$, and (AgBi)$_{0.5}$-MoO$_4$.

Photocatalytic activities of scheelite-type molybdates and tungstates for H$_2$ or O$_2$ evolution from an aqueous solution containing a sacrificial reagent are listed in Table 1. All molybdates hardly produce H$_2$. (NaBi)$_{0.5}$MoO$_4$ and (AgBi)$_{0.5}$MoO$_4$ possessing the characteristic valence bands showed the photocatalytic activities for O$_2$ evolution. It indicates that their valence bands have potentials deep enough to produce O$_2$ and that these materials have surface active sites for O$_2$ formation. In the case of tungstates, (NaBi)$_{0.5}$WO$_4$ produced H$_2$. It indicates that the con-

duction band consisting of W5d orbitals in a scheelite structure possesses a negative potential enough to produce H$_2$. However, (AgBi)$_{0.5}$WO$_4$ showed a negligible activity for H$_2$ evolution. It is due to that the conduction band of (AgBi)$_{0.5}$WO$_4$ with a structure different from scheelite does not have a satisfying potential for H$_2$ production even if the band is formed by the W5d orbitals as well as (NaBi)$_{0.5}$WO$_4$. In addition, Ag$^+$ and/or Bi^{3+} ions may form trap sites of photogenerated electrons.

The number of heterogeneous photocatalysts based on W and Mo for H$_2$ or O$_2$ evolution was quite small. Moreover, the scheelite-type photocatalysts were limited to only PbMoO$_4$[17] and BiVO$_4$.[16] In the present study, it has been found that some scheelite-type molybdates and tungstates function as photocatalysts for H$_2$ or O$_2$ evolution in the presence of sacrificial reagents. Bi6s and Ag4d have been proven to be effective orbitals to form the valence band more negatively than O2p.

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