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Photocatalytic Properties of Ordered Double Perovskite Oxides

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Ordered double perovskite oxides ($A_2BB'O_6$, $AA'BB'O_6$) which contained W, Ta, Nb and Ti were synthesized, and the applicability of the oxides to photocatalytic reaction was discussed. The stability of the oxides strongly depended on the constituent atoms, especially B-site cations. Ta-, Nb- and Ti-containing perovskites were stable under two types of photocatalytic reaction conditions, namely, H_2 evolution from aqueous methanol solution and O_2 evolution in Ag^+ ion-containing aqueous solution. Among the perovskite oxides, La_2ZnTiO_6 showed catalytic activity for the latter reaction and the rate for O_2 evolution normalized by catalyst surface area was one third of that of TiO_2.

1. Introduction

Photocatalytic reactions over semiconductors have attracted much attention over several decades because they can utilize solar energy for chemical reactions such as overall water splitting[1,2]. Photocatalytic events in semiconductor are undertaken by absorption of near UV or visible light to generate excited electron-hole pairs, and these species migrate to catalyst surface and result in redox reactions. The charge separation process, one of the most important steps in photocatalytic reaction, strongly depends on the crystal structure and the constituent elements in the catalyst.

So far, many photocatalysts have been developed with different crystal structures, and most of them contain W^{6+}, Ta^{5+}, Nb^{5+} and Ti^{4+} cations because these species are effective in obtaining photocatalytic activities[1,2].

Perovskite-type oxide has general formula of $A^{n+}B^{m+}O_3$ ($n + m = 6$), and most of metal cations are known to be stably incorporated in the structure. Perovskite-type oxides are also possible candidates for photocatalytic materials, and several kinds of perovskite-type oxides such as $A^+B^{5+}O_3$ (A^+ = Ag, Li, Na, K, B^{5+} = Ta, Nb)[3,4] and $A^{2+}In_{0.5}Nb_{0.5}O_3$ (A^{2+} = Ba, Sr, Ca)[5] have been reported to be active for photocatalytic reactions.

Ordered double perovskite ($A_2BB'O_6$, $AA'BB'O_6$) is well known as a subclass of perovskite-type oxide. In the structure, two kinds of metal cations occupy B-site in the same molar ratio, and the metal cations arrange alternately at B-site[6]. The most favorable arrangement is the rock-salt ordering as shown in Fig. 1[7], and in addition to Ta^{5+}, Nb^{5+} and Ti^{4+} cations, W^{6+} cation is also possible to be stably incorporated in ordered double perovskite[6, 8].

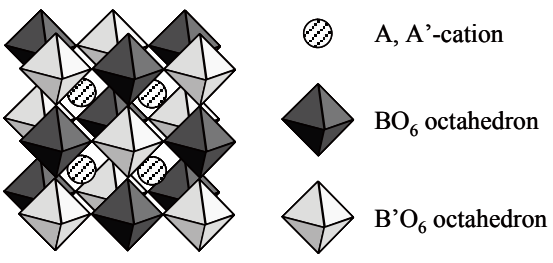

Fig. 1 Crystal structure of ordered double perovskite with rock-salt ordering of B-cations.

In the present study, ordered double perovskites which contain W^{6+}, Ta^{5+}, Nb^{5+} and Ti^{4+} cations at B-sties have been synthesized and their photocatalytic properties under UV-light irradiation have been investigated. Photocatalytic H_2 production from aqueous methanol solution and O_2 evolution from Ag ion-containing aqueous solution were used to investigate activities of photogenerated electron and hole, respectively. From the results of photocatalytic activity, the applicability of the ordered double perovskites to photocatalytic reactions was discussed from the standpoint of catalyst stability and activity.

2. Experimental

2.1 Preparation and characterization of perovskite oxides

Polycrystalline powders of perovskite-type oxides were synthesized by a conventional solid-state reaction. The starting materials are listed in the footnote of Table 1. The materials were adequately mixed in the stoichiometoric ratio by a pestle and mortar and then by a universal ball mill. The mixture was calcined under the conditions which are also shown in Table 1. TiO_2 (JRC-TIO-4, identical to P25, S_{BET} = 55 m^2/g) was supplied from Catalysis Society of Japan and used as a reference photocatalyst.

The crystal structures of samples thus prepared were examined by powder XRD measurement using Cu-Kα irradiation (Rigaku, RINT-2200) and were refined by Rietveld method using RIETAN-2000 program[9]. The surface area of a sample was determined by BET method from N_2 adsorption isotherm at 77 K (BEL JAPAN, Inc., BELSORP-mini). Diffuse reflectance (DR) UV-VIS spectra of samples were measured using Shimadzu UV-3100 spectrophotometer equipped with an integrating sphere attachment. α-Al_2O_3 powder was used as a reference sample. The mixture of prepared sample and Al_2O_3 powder was used to obtain a reflectance spectrum, and the spectrum was transformed into the Kubelka-Munk function.

Table 1 Synthesis conditions and crystal structures of ordered double perovskites synthesized in this study

Compound [a)]	Calcination condition	Cell parameter (a, b, c / nm, β / °)
Ba_2CoWO_6	1100 °C, 10 h	a = 0.810621(6)
Ba_2NiWO_6	1100 °C, 10 h	a = 0.806676(6)
Ba_2CuWO_6	1000 °C, 5 h	a = 0.55668(3), c = 0.86289(5)
Ba_2ZnWO_6	1100 °C, 10 h	a = 0.812161(6)
Sr_2CoWO_6	1200 °C, 20 h	a = 0.558195(5), c = 0.798172(8)
Sr_2NiWO_6	1100 °C, 5 h	a = 0.555965(4), c = 0.791745(7)
Sr_2CuWO_6	1000 °C, 5 h	a = 0.54283(1), c = 0.84131(2)
Sr_2ZnWO_6	1100 °C, 20 h	a = 0.56321(4), b = 0.56089(3), c = 0.79235(4), β = 89.99(3)
$LaBaCoTaO_6$ [b)]	1300 °C, 20 h	a = 0.8067(1)
$LaBaNiTaO_6$ [b)]	1300 °C, 20 h	a = 0.8024(1)
$LaBaCoNbO_6$ [b)]	1300 °C, 20 h	a = 0.8068(1)
$LaBaNiNbO_6$ [b)]	1300 °C, 20 h	a = 0.8032(1)
$LaBaZnNbO_6$ [b)]	1200 °C, 50 h	a = 0.80863(5)
La_2ZnTiO_6	1200 °C, 20 h	a = 0.55746(1), b = 0.56167(1), c = 0.78922(2), β = 90.01(1)

a) Starting material (purity, origin); La_2O_3 (>99.99%, KI), $BaCO_3$ (>99%, KI), $SrCO_3$ (>99.9%, KA), Co_3O_4 (>99.9%, KO), NiO (>98%, KI), CuO (>99%, KI), ZnO (>99.5%, KI), WO_3 (>99.9%, KI), Ta_2O_5 (>99.9%, W), Nb_2O_5 (>99.9%, KI), TiO_2 (>98%, KI), Origin: KI; Kishida Chem. Co., Ltd., KA; Kanto Chem. Co., Inc., KO; Kojundo Chem. Lab. Co., Ltd., W; Wako Pure Chem. Industries.

b) Cell parameters were determined from the analysis of PXRD patterns. Those of the other samples were determined by Rietveld refinement.

2.2 Catalyst stability test

Stability of catalyst samples under photoirradiation was investigated in methanol-water solution (50 vol%) and aqueous solution which contained 0.02 M $AgNO_3$. Catalyst sample (50 mg) was dispersed into the solution (45 mL) and the suspension was transferred to a reaction cell made of Pyrex glass and was stirred by a magnetic stirrer. After deaeration of the suspension with Ar, UV light was irradiated with a 500 W high-pressure mercury lamp for 5 h. After the photoirradiation, the suspension was filtered, and the obtained powder was dried. The crystal structure of the powder was examined by PXRD measurement.

2.3 Photocatalytic activity measurement

Photocatalytic activity of a catalyst was examined by a gas-closed circulation system equipped with a GC-TCD (Shimadzu, GC-8A). Catalyst sample (0.3-0.5 g) was dispersed into 500 mL of 0.01 M AgF aqueous solution in an inner-irradiation-type reaction cell made of Pyrex glass. The reaction cell was connected to the gas-closed circulation system, and then the suspension was deaerated with stirring by a magnetic stirrer. After the introduction of He gas, UV light was irradiated with a 100 W high-pressure mercury lamp, and the amount of O_2 evolved was quantified by GC. After the reaction, the amount of Ag deposition was quantified by ICP measurement (Seiko Instruments Inc., SPS1700). The catalyst surface after the photoreaction was examined by means of SEM-EDX observation (Hitach Science Systems, Ltd., SEMEDX TypeN).

3. Results and discussion

3.1 Structural analysis

Table 1 summarizes the synthesis conditions and crystal structures of double perovskites tested in this study. The calcination conditions were optimized to minimize the amount of impurity phases for all the perovskite oxides. For W- and Ti-containing double perovskites, the lattice parameters and the cation arrangements of the ordered double perovskites were consistent with those in the previous reports[10-13)]. Rietveld analyses confirmed that these compounds had the rock-salt arrangement of B-cations in the crystal structures.

In this study, we newly synthesized perovskite oxides, $LaBaB^{2+}B'^{5+}O_6$ (B^{2+} = Co, Ni, B'^{5+} = Ta, Nb) and $LaBaZnNbO_6$. The characteristic diffraction lines from cubic perovskite-type structure were observed in their PXRD patterns (data are not shown). Concerning the cubic double perovskite, superlattice structure with a unit cell of $2a_p \times 2a_p \times 2a_p$, where a_p is a lattice constant of primitive cubic ABO_3 type perovskite, is formed due to the alternate arrangement of B-cations. Therefore, superlattice diffraction lines appear in the PXRD patterns for these perovskites[6)]. The superlattice diffraction lines were clearly observed in the PXRD patterns of the Ta-

and Nb-containing double perovskites, indicating that the rock-salt arrangement of B-cations was also formed in crystal structures of these samples.

3.2 Stability of ordered double perovskite under photocatalytic conditions

It has been reported that ZnO suffers photocorrosion when it is used in liquid-solid heterogeneous photoreaction[14], in marked contrast with TiO_2 which showed high stability under the various photoreaction conditions. Also, W-oxides easily decomposed to form soluble tungstate species in alkali media. Therefore, it is indispensable to investigate the catalyst stability of the perovskite oxides under the photoreaction conditions. Table 2 shows the stabilities of the W-, Ta-, Nb- and Ti-containing ordered double perovskites in aqueous methanol solution and $AgNO_3$-containing aqueous solution under photoirradiation. After the photoirradiation in the aqueous methanol solution, $A^{2+}WO_4$ (A^{2+} = Ba, Sr,) and the other crystal phases were detected by PXRD measurement for $A^{2+}{}_2B^{2+}WO_6$ (A^{2+} = Ba, Sr, B^{2+} = Cu, Zn), and only the diffraction lines from perovskite phase were observed for $A^{2+}{}_2B^{2+}WO_6$ (A^{2+} = Ba, Sr, B^{2+} = Co, Ni), indicating that Co/W and Ni/W systems were stable and Cu/W and Zn/W systems were unstable under the condition. For $A^{2+}{}_2B^{2+}WO_6$ (A^{2+} = Ba, Sr, B^{2+} = Co, Ni), however, diffraction lines from Ag_2WO_4 (and Ag_2O) in addition to perovskite phase were observed after photoirradiation in the $AgNO_3$-containing aqueous solution. Thus, these perovskites were decomposed under the reaction conditions. These findings suggested that W-containing perovskites were not suitable for the photocatalytic reaction in aqueous media because of their low stability.

As for the Ta-, Nb- and Ti-containing ordered double perovskites, on the other hand, no differences in the crystal structures were observed before and after photoirradiation in both of the aqueous solutions, indicating the high stability of the oxides under the conditions without the photocorrosion of Ti and Zn oxides. The results suggested the stability of ordered double perovskite depended strongly on the nature of high valence B-cation.

3.3 Photocatalytic activity of La_2ZnTiO_6

Catalytic test reaction was conducted with the perovskite oxides synthesized in this study, and our study revealed that La_2ZnTiO_6 showed the activity for O_2 evolution from Ag^+ ion-containing aqueous solution. The reaction mechanism on semiconductor photocatalysts, such as TiO_2 has been well studied and the reaction pathway can be expressed in eqs.(1)-(3).

$$\text{null} \xrightarrow{h\nu} e^- + h^+ \quad \ldots(1)$$

$$Ag^+ + e^- \rightarrow Ag^0 \quad \ldots(2)$$

$$2H_2O + 4h^+ \rightarrow O_2 + 2H^+ \quad \ldots(3)$$

Here, e^-, and h^+ refer to excited electron and hole, respectively. The excited electron reduces Ag^+ ion to Ag^0 metal and hole oxidizes water to form O_2.

Table 2 Stability of ordered double perovskite under photoirradiation in methanol and $AgNO_3$ aqueous solutions [a]

	In a methanol aqueous solution	In an $AgNO_3$ aqueous solution
Compound	Stability [a]	Stability [a]
Ba_2CoWO_6	Stable	Ba_2CoWO_6, Ag_2WO_4
Ba_2NiWO_6	Stable	Ba_2NiWO_6, Ag_2WO_4, Ag_2O
Ba_2CuWO_6	Ba_2CuWO_6, $BaWO_4$	-
Ba_2ZnWO_6	$BaWO_4$, ZnO	-
Sr_2CoWO_6	Stable	Sr_2CoWO_6, Ag_2WO_4
Sr_2NiWO_6	Stable	Sr_2NiWO_6, Ag_2WO_4, Ag_2O
Sr_2CuWO_6	$SrWO_4$, CuO	-
Sr_2ZnWO_6	$SrWO_4$, ZnO	-
$LaBaCoTaO_6$	Stable	Stable
$LaBaNiTaO_6$	Stable	Stable
$LaBaCoNbO_6$	-	Stable
$LaBaNiNbO_6$	-	Stable
$LaBaZnNbO_6$	-	Stable
La_2ZnTiO_6	Stable	Stable

a) Stability was examined by PXRD patterns before and after photoirradiation in aqueous solutions of methanol and $AgNO_3$.

Fig. 2 shows the time course for O_2 evolution from a 0.01 M AgF aqueous solution over La_2ZnTiO_6. The amount of O_2 evolved increased with time up to 8 h, and then the O_2 evolution stopped in dark, indicating that the O_2 evolution photocatalytically proceeded over La_2ZnTiO_6. The activity for O_2 evolution over commonly used TiO_2 (P 25) was investigated and compared with that of La_2ZnTiO_6 (Table 3). The total amount of O_2 evolved over La_2ZnTiO_6 was quite lower than that over TiO_2, but the amount of O_2 normalized by catalyst surface area was one third of that of TiO_2.

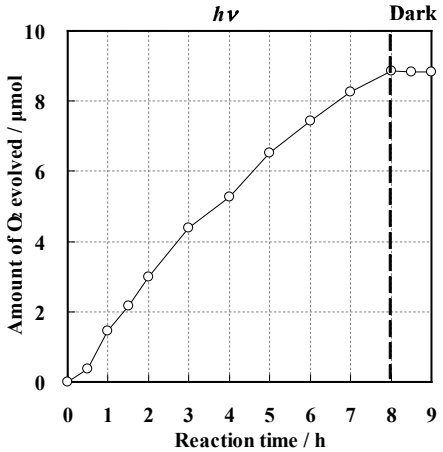

Fig. 2 Time course of O_2 evolution from a 0.01 M AgF aqueous solution over La_2ZnTiO_6 (0.5 g).

PXRD studies confirmed that the reduction of Ag^+ to Ag^0 proceeded on La_2ZnTiO_6 catalyst during the photoirradiation in Ag^+-containing aqueous solution. Fig. 3 shows the PXRD patterns of the catalyst used for the reaction. A characteristic XRD peak for Ag^0 was observed at $2\theta = 38.2$ degree. The SEM-EDX observation further provided the evidence for formation of Ag^0 metal species on the catalyst surface. As shown in Fig. 4, deposition of rod-shape Ag metal over La_2ZnTiO_6 was observed, which further supported that the Ag reduction (eq.(2)) proceeded on the catalyst surface.

Table 3 also summarizes the results for the quantification of Ag metal deposited on La_2ZnTiO_6 after the reaction. According to the stoichiometry in eqs.(1)-(3), the theoretical molar ratio of Ag to O_2 is 4.0. For La_2ZnTiO_6, the ratio of Ag/O_2 showed 5.7 and was deviated from the theoretical value. As for the

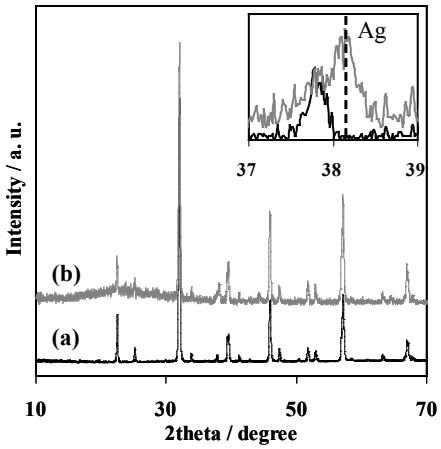

Fig. 3 PXRD patterns of La_2ZnTiO_6 (a) before and (b) after photoirradiation in a 0.02 M $AgNO_3$ aqueous solution

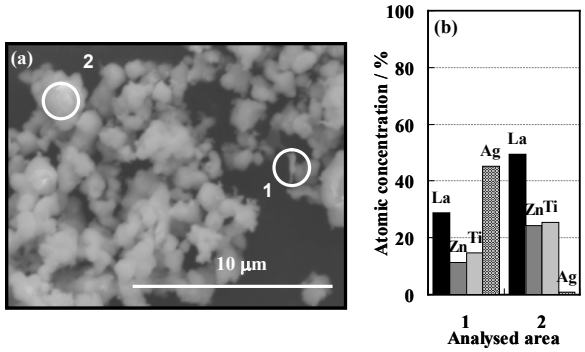

Fig. 4 SEM image (a) and results of the elemental analysis (b) of La_2ZnTiO_6 after photoirradiation in a 0.02 M $AgNO_3$ aqueous solution.

photocatalytic O_2 evolution over TiO_2 in an AgF aqueous solution, Nishimoto *et al*. has reported that the ratio of Ag/O_2 was larger than 4.0 due to the adsorption of evolved O_2 on the photocatalyst[15]. If one considers that O_2 adsorbs on the surface B-cations (Zn^{2+}, Ti^{4+}) in the ratio of 1:1 for La_2ZnTiO_6, the amount of O_2 adsorbed on the catalyst is estimated to be 2.4 μmol assuming $10\bar{1}$ crystal plane. When this value is taken into account, the ratio of Ag/O_2 is 4.5 and became closer to the theoretical value of 4.0.

Fig. 5 shows the DR UV-VIS spectra of La_2ZnTiO_6 and TiO_2 P25. The absorption edge for La_2ZnTiO_6 was

Table 3 Photocatalytic activity of La_2ZnTiO_6 and TiO_2 for O_2 evolution from a 0.01 M AgF aqueous solution

Sample	Specific surface area / $m^2\ g^{-1}$	O_2 evolution [a]		Amount of Ag deposited / μmol [c]	Ratio of Ag/O_2
		μmol [b]	μmol $(m^2_{-cat})^{-1}$		
La_2ZnTiO_6	0.8	8.9	22.3	51	5.7
TiO_2	55.3	1153.8	69.5	-	-

a) 0.5 g of La_2ZnTiO_6 and 0.3 g of TiO_2 were used for the reaction, b) amount of gas evolved after 8 h photoirradiation, c) quantified by ICP measurement.

observed at shorter wavelength than that for TiO_2. Optical band gap of La_2ZnTiO_6 was estimated from the spectra by extrapolating the linier portion to *x* axis, and the gap was 3.9 eV. This value was much larger than that of TiO_2 3.3 eV estimated from the spectrum. TiO_2 (P 25) is well known as the mixture of anatase and rutile phases in the ratio of 80% and 20%, respectively. Therefore, the optical property of TiO_2 (P 25) is governed by that of the major phase, and the gap is close to that of anatase phase (3.2 eV)[2]. DR UV-VIS spectrum of La_2ZnTiO_6 suggested the absence of unreacted TiO_2, because it did not absorb light longer than about 350 nm. This excludes the possibility that impurity TiO_2 acted as the photocatalyst for the reaction and ensures the occurrence of photocatalytic O_2 evolution over La_2ZnTiO_6. La_2ZnTiO_6 showed almost no activity for H_2 generation in aqueous methanol solution. This can be ascribed to the lack of H_2 generation sites, such as Pt, Rh, and RuO_x on the surface of La_2ZnTiO_6 perovskite.

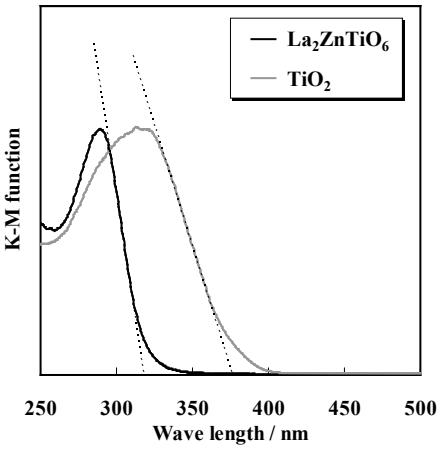

Fig. 5 Absorption spectra of La_2ZnTiO_6 and TiO_2.

4. Conclusions

To investigate the applicability of the W-, Ta-, Nb- and Ti-containing ordered double perovskite to photocatalytic reactions, 14 kinds of ordered double perovskites were systematically synthesized and characterized by PXRD measurements. The W-containing ordered double perovskites decomposed under the photoreaction conditions, photoirradiation in aqueous methanol solution or in Ag^+ ion-containing aqueous solution. On the other hand, Ta-, Nb- and Ti-containing ordered double perovskites were stable under the same conditions, indicating that the stability of ordered double perovskite depended mostly on the nature of high valence B-cation.

Among the perovskite oxides tested in this study, La_2ZnTiO_6 showed the activity for O_2 evolution and Ag reduction. The reduction of Ag^+ ion to Ag^0 on the surface was confirmed by PXRD and SEM-EDX studies. The activity of La_2ZnTiO_6 for Ag reduction normalized by the catalyst surface area was one third of that of TiO_2.

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