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Some structural and photophysical properties of two functional double oxides Bi_2MTaO_7 (M = Ga and In)

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Abstract

Two new functional double oxides, Bi_2MTaO_7 (M = Ga and In), were synthesized by the conventional solid-state reaction method. They were characterized by the Rietveld structural analysis and UV-Vis diffuse reflectance spectroscopy. Bi_2MTaO_7 have distorted pyrochlore-type structure. The lattice distortion of Bi_2InTaO_7 (0.067) is larger than that of Bi_2GaTaO_7 (0.039). The angle between the corner-linked MO_6 octahedral in Bi_2InTaO_7 (143.4°) is closer to 180° than that of Bi_2GaTaO_7 (128.3°). The abilities of the H_2 and O_2 evolution over Bi_2MTaO_7 were evaluated from an aqueous CH_3OH solution and an aqueous $Ce(SO_4)_2$ solution under UV light irradiation, respectively. The rates of the H_2 and O_2 evolution over Bi_2InTaO_7 were clearly larger than that of Bi_2GaTaO_7 . These results suggest that the abilities of the H_2 and O_2 evolution might be correlated with the lattice distortions and the angles between the corner-linked MO_6 octahedral in Bi_2MTaO_7 . (© 2004 Elsevier B.V. All rights reserved.

Keywords: Bi2MTaO7; Pyrochlore-type structure; Photophysical property; UV light irradiation; H2 and O2 evolution

1. Introduction

Functional Bi₂MNbO₇ (M = Al, Ga, In, and Fe) and Bi₂RNbO₇ (R = rare earth ions) double oxides with a distorted pyrochlore-type structure have been reported by Zou et al. [1–3]. Crystal structures and some photophysical properties, such as the abilities of the H₂ and O₂ evolution over Bi₂MNbO₇ and Bi₂RNbO₇ under UV light irradiation, are clearly changed with the change of M or R. This indicates that the different M or R are possible to modify their crystal and electronic structures, then lead to the difference in the abilities of the H₂ and O₂ evolution under UV light irradiation.

In this study, two new functional double oxides, Bi_2 MTaO₇ (M = Ga and In), were successfully synthesized by substituting Nb by Ta in Bi₂MNbO₇. Bi₂MTaO₇ were characterized by the Rietveld structural analysis and UV-Vis diffuse reflectance spectroscopy. The abilities of the H₂ and O₂ evolution over Bi₂MTaO₇ were evaluated from an aqueous CH₃OH solution and an aqueous Ce(SO₄)₂ solution under UV light irradiation, respectively. The results indicated that the ability of the H₂ evolution over Bi₂InTaO₇ is the largest among Bi₂MTaO₇ and Bi₂MNbO₇. Here, syntheses, crystal structures and some photophysical properties of the two new functional double oxides, Bi₂MTaO₇ (M = Ga and In), are reported.

2. Experimental

2.1. Sample preparation

The polycrystalline samples of Bi₂MTaO₇ were prepared by the conventional solid-state reaction method. The starting materials, Bi₂(CO₃)O₂, M₂O₃ (M = Ga and In) and Ta₂O₅ with purity of high grade, were purchased from Wako Pure Chem. M₂O₃ (M = Ga and In) and Ta₂O₅ were dried at 873 K before use. The stoichiometric amounts of the starting materials were weighed accurately and mixed intimately. The precursors were sintered in alumina crucible in air and analyzed by powder X-ray diffraction (XRD) measurement. As a result, Bi₂InTaO₇ was synthesized at 1323 K and Bi₂GaTaO₇ was synthesized at 1353 K for 30 h, respectively.

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2.2. Crystal structure

The crystal structure of Bi₂MTaO₇ were determined by the Rietveld structure refinement. A conventional JDX-3500 diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å) was used for the measurements of their XRD patterns. The XRD data were collected with a step scan procedure in $2\theta =$ $5-100^{\circ}$. The step interval was 0.024° and scan speed, 1° per minute. Full-profile structure refinements of the collected powder diffraction data for Bi₂MTaO₇ were performed by the Rietveld program RIETAN 97 β [4].

2.3. Photophysical property

The UV-Vis diffuse reflectance spectra of Bi_2MTaO_7 were measured by an UV-Vis spectrometer (Shimadzu UV-2500) with $BaSO_4$ as a reference at room temperature and were converted from reflection to absorbance by the Kubella–Munk method.

The reactions of the H₂ and O₂ evolution over Bi₂MTaO₇ were carried out by a gas-closed circulation system and an inner-irradiation type quartz cell with a 400 W high-pressure Hg lamp (Riko-Kagaku Co. Ltd., Japan). The samples were stirred by a magnetic stirrer and then suspended in an aqueous CH₃OH solution for the H₂ evolution and an aqueous Ce(SO₄)₂ solution for the O₂ evolution. The gases evolved were measured with a thermal conductivity detector (TCD) gas chromatograph (Shimadzu GC-8AIT), which was connected to a gas circulating line.

Evaluation of the H₂ and O₂ evolution was performed in an aqueous CH₃OH solution (Powder sample: 2.0 g; CH₃OH: 50 cm³; pure H₂O: 320 cm³; 0.2 wt.% Pt) and an aqueous Ce(SO₄)₂ solution (Powder sample: 1.0 g; Ce(SO₄)₂·4H₂O: 1.0 mmol; pure H₂O: 370 cm³), respectively. The Pt metal powder was loaded on the surface of the samples by photodeposition of H₂PtCl₆·6H₂O, CH₃OH, and Ce(SO₄)₂·4H₂O were used as sacrificial reagents. Under light irradiation, methanol, as a reducing reagent, can promote a H₂ evolution reaction in an aqueous CH₃OH solution; cerium sulfate tetrahydrate, as being an oxidizing reagent, can promote an O_2 evolution reaction in aqueous $Ce(SO_4)_2$ solution [5].

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the XRD patterns of Bi₂MTaO₇. Although Bi₂MTaO₇ show the similar XRD patterns, the 2θ angles of reflections are clearly different. Therefore, the lattice parameters of Bi₂MTaO₇ are different. Fig. 2 shows the result of the Rietveld structure refinement for Bi₂InTaO₇. This result is similar to that of the Rietveld structure refinement for Bi₂GaTaO₇. The final positional and isotropic thermal parameters are shown in Table 1. The positional and isotropic thermal parameters of all atoms in Bi₂MTaO₇ were refined separately. The refinements yielded *R* factors, *R*_I = 5.45%, *R*_p = 7.60%, *R*_{wp} = 12.55% for Bi₂GaTaO₇ in space group *Fd3m*.



Fig. 1. Powder X-ray diffraction patterns for Bi_2GaTaO_7 (a) and Bi_2InTaO_7 (b) with a distorted pyrochlore-type structure.



Fig. 2. Result of the Rietveld structure refinement of the X-ray diffraction patterns for Bi₂InTaO₇ (Plus marks: observed; solid line: calculated; $R_{\rm I} = 4.80\%$, $R_{\rm p} = 6.85\%$, $R_{\rm wp} = 11.42\%$).

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Table 1 Final structural parameters of Bi_2MTaO_7 (M = Ga and In) obtained by the Rietveld structure refinement

Atom	x	y z		Beq
Bi ₂ GaTaO ₇	1			
Bi	0.500	0.500	0.500	3.5
Ga	0.000	0.000	0.000	0.6
O_1	0.336(2)	0.125	1.5	
O_2	0.375	0.375	0.375	1.0
Та	0.000	0.000	0.000	0.6
Bi ₂ InTaO ₇				
Bi	0.500	0.500	0.500	3.1
In	0.000	0.000	0.000	0.5
O_1	0.308(2)	0.125	1.6	
O ₂	0.375	0.375	0.375	1.0
Та	0.000	0.000	0.000	0.5

The outcomes of the final refinement indicate that Bi_2MTaO_7 have distorted pyochlore-type structure, cubic system with space group Fd3m and their lattice parameters are a = 10.4478(3) Å for Bi_2GaTaO_7 and a = 10.7612(2) Å for Bi_2InTaO_7 . All of the reflection peaks can be successfully indexed based on the lattice parameter and the space group (see Fig. 1). Although Bi_2MTaO_7 can crystallize into the similar distorted pyrochlore-type structure (Cubic, space group Fd3m), the lattice parameter of Bi_2GaTaO_7 is clearly smaller than that of Bi_2InTaO_7 because M^{3+} (M = Ga and In) ions have different effective ionic radii, i.e., Ga^{3+} (0.620 Å) $< In^{3+}$ (0.800 Å) [6].

The x structural parameters of O_1 are 0.336(2) for Bi₂GaTaO₇ and 0.308(2) for Bi₂InTaO₇ as listed in Table 1. The x structural parameter is an index of the structure's variation on the pyrochlore-type A₂B₂O₇ double oxides (Cubic, space group Fd3m) and is equal to 0.375 when the six O1 atoms are located on the position of the related fluorite-type double oxides [7]. Therefore, information on the lattice distortion can be obtained from the x structural parameters. The lattice distortion of Bi₂InTaO₇ is larger than that of Bi_2GaTaO_7 because deviation of the x structural parameter compared with 0.375 for Bi_2InTaO_7 (0.067) is larger than that for Bi₂GaTaO₇ (0.039). Charge separation is demanded to prevent recombination of the photoinduced electrons and holes in the reactions of the H_2 and O_2 evolution under UV light irradiation. The lattice distortion is considered beneficial to separate the photoinduced electrons and holes. Therefore, the larger the lattice distortion is, the higher the ability of the H_2 and O_2 evolution might be expected.

Fig. 3 shows the schematic structural diagram of Bi_2MTaO_7 . Bi_2MTaO_7 consist of a three-dimensional network structure of corner-linked MO_6 (M = Ga, In and Ta) octahedral. The MO_6 octahedral are connected into chains by Bi ions. Selected bond lengths and angles are listed in Table 2. The six Bi–O1 bond lengths are longer than those of the two Bi–O₂ bond lengths. The Ga(Ta)–O1 bond lengths (2.053 Å) of Bi₂GaTaO₇ are longer than the In(Ta)–O1 bond lengths (2.004 Å) of Bi₂InTaO₇. The Ga(Ta)–O1–Ga(Ta) bond angles (128.3°) of Bi₂GaTaO₇ are



Fig. 3. Schematic structural diagram of Bi_2MTaO_7 (M = Ga and In). Bi_2MTaO_7 consist of a three-dimensional network structure of corner-linked MO₆ (M = Ga, In and Ta) octahedral.

smaller than the In(Ta)–O1–In(Ta) bond angles (143.3°) of Bi₂InTaO₇. It is obvious that not only the lattice parameters but also the M–O1, Bi–O1, Bi–O₂ bond lengths and M–O1–M bond angles are changed when Ga is substituted by In in Bi₂MTaO₇.

The angle between the corner-linked MO_6 octahedral, i.e., the M–O1–M bond angle of Bi₂InTaO₇ (143.3°) is closer to 180° than that of Bi₂GaTaO₇ (128.3°). Wiegel et al. [8] pointed out that the closer the bond angle of M–O1–M is to 180°, the more the excited state is delocalized. That is to say, the photoinduced electrons and holes in Bi₂InTaO₇ should be moved more easily than those in Bi₂GaTaO₇. The mobility of the photoinduced electrons and holes affect the ability of H₂ and O₂ evolution because it affects the probability of electrons and holes to reach reaction sites on the sample surface.

3.2. Some photophysical property

Fig. 4 shows the UV-Vis diffuse reflectance spectra of Bi₂MTaO₇. Bi₂MTaO₇ show photo-absorption not only in the UV light region but also in the visible light region ($\lambda >$

Table 2

Selected bond lengths (Å) and bond angles (°) of Bi_2MTaO_7 (M = Ga and In) obtained by the Rietveld structure refinement

	Bi ₂ GaTaO ₇	Bi ₂ InTaO ₇
Bi–O ₁	2.521	2.805
Bi-O ₂	2.262	2.330
M-O ₁	2.053	2.004
Mean Bi-O	2.391	2.567
$M - O_1 - M$	128.3	143.4



Fig. 4. UV-Vis diffuse reflectance spectra of Bi_2MTaO_7 (M = Ga and In).

400 nm) though the photo-absorption in the visible light region is weak. Compared with Bi₂InTaO₇, the onset of Bi₂GaTaO₇ is shifted to shorter wavelength side, indicating a wider energy gap than that of Bi₂InTaO₇. Their energy gaps, estimated by plots of the square root of Kubelra–Munk functions F(R) against photon energy [9], are 3.0(2) eV for Bi₂GaTaO₇ and 2.9(1) eV for Bi₂InTaO₇. Figs. 5 and 6 shows the results of the H₂ and O₂ evolutions from an aqueous CH₃OH solution and an aqueous Ce(SO₄)₂ solution under UV light irradiation over Bi₂MTaO₇, respectively. Rates of the H₂ and O₂ evolutions and some physical properties were listed in Table 3. For a comparison, the results of the H₂ and O₂ evolution on the reported Bi₂MNbO₇ (M = Ga and In) double oxides were also included in Table 3 [2].

The rates of the H₂ evolution were estimated to be $0.11 \text{ mmol }h^{-1}$ for Bi₂GaTaO₇ and $0.99 \text{ mmol }h^{-1}$ for Bi₂InTaO₇ in the first 10 h. The rate of the H₂ evolution for Bi₂InTaO₇ is significantly higher than that of Bi₂GaTaO₇. This is consistent with the expectation from their structural



Fig. 5. Results of the H_2 evolution over Bi_2MTaO_7 (M = Ga and In) from an aqueous CH₃OH solution under UV light irradiation (Sample: 2.0 g; CH₃OH: 50 cm³; pure H₂O: 320 cm³; 0.2 wt.% Pt; light source: 400 W high-pressure Hg lamp).



Fig. 6. Results of the O_2 evolution over Bi_2MTaO_7 (M = Ga and In) from an aqueous Ce(SO₄)₂ solution under UV light irradiation (Sample: 1.0 g; Ce(SO₄)₂: 1 mmol; pure H₂O: 370 cm³; light source: 400 W high-pressure Hg lamp).

feature as described above. The ability of the H₂ evolution for Bi₂InTaO₇ is larger than that of Bi₂GaTaO₇ since the lattice distortion of Bi₂InTaO₇ is larger than that of Bi₂GaTaO₇ and the angle between the corner-linked MO₆ octahedral for Bi₂InTaO₇ is closer to 180 than that of Bi₂GaTaO₇. Moreover, the rate of the H₂ evolution over Bi₂InTaO₇ is also higher than that of the reported Bi₂MNbO₇ (M = Ga and In) double oxides. The rates of the O₂ evolution were estimated to be 0.005 mmol h⁻¹ for Bi₂GaTaO₇ and 0.01 mmol h⁻¹ for Bi₂InTaO₇ in the first 10 h as listed in Table 3.

The effect of UV light irradiation was also observed by light on/off shutter studies. The H₂ evolution stopped when the UV light irradiation was terminated. This phenomenon showed that the reaction of the H₂ evolution was induced by the UV light irradiation. The similar rate was produced after the system was evacuated. Meanwhile, the stabilities of Bi₂MTaO₇ were checked by XRD analysis. Bi₂MTaO₇ are stable under the UV light irradiation since no change can be found in their XRD patterns before and after the reactions.

Table 3

Some physical properties and the rates of the H_2 and O_2 evolution from an aqueous CH_3OH solution and an aqueous $Ce(SO_4)_2$ solution over Bi_2MTaO_7 and the reported Bi_2MNbO_7 (M = Ga and In) double oxides

	-	-			
Double oxide	Lattice parameter (Å) ^a	Band gap (eV)	Rate of gas evolution $(\text{mmol } h^{-1})^b$		
			H ₂ ^c	O ₂	
Bi2GaTaO7	10.4478(3)	3.0	0.11	0.005	This study
Bi ₂ InTaO ₇	10.7612(2)	2.9	0.99	0.01	This study
Bi2GaNbO7	10.7342(2)	2.8	0.30	0.01	[2]
Bi ₂ InNbO ₇	10.7793(2)	2.7	0.18	0.007	[2]

^a The cubic system with space group Fd3m was obtained by the Rietveld structure refinement.

^b Measured in an inner-irradiation quartz cell irradiated by a 400 W high-pressure Hg lamp.

 $^{\rm c}$ Pt was loaded on the surface of powder sample (Sample: 2.0g; CH₃OH: 50 cm³; pure H₂O: 320 cm³; 0.2 wt.% Pt).

4. Conclusion

The Rietveld structural analysis indicate that Bi_2MTaO_7 (M = Ga and In) consist of a three-dimensional network structure of corner-linked MO₆ (M = Ga, In, and Ta) octahedral. The lattice parameters, lattice distortions and the angles between the corner-linked MO₆ octahedral are different due to the different effective ionic radii of M³⁺ (M = Ga and In).

Bi₂MTaO₇ show photo-absorption not only in the UV light region but also in the visible light region ($\lambda > 400$ nm) though the photo-absorption in the visible light region is weak. The energy gaps of Bi₂MTaO₇ were estimated to be 3.0(2) eV for Bi₂GaTaO₇ and 2.9(1) eV for Bi₂InTaO₇. The ability of the H₂ evolution over Bi₂InTaO₇ from an aqueous CH₃OH solution under UV light irradiation was clearly larger than that of Bi₂GaTaO₇ and the reported Bi₂MNbO₇ double oxides. These results suggest that the abilities of the H_2 and O_2 evolution over Bi_2MTaO_7 might be correlated with the lattice distortions and the angles between the corner-linked MO_6 octahedral.

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