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Effect of Zr substitution for Ti in $KLaTiO_4$ for photocatalytic water splitting

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The effect of substitution of Zr for Ti in $KLaTiO_4$ with a layered perovskite structure has been studied on the photocatalytic decomposition of water under the UV light irradiation. Both the optical property and the crystallinity of $KLaTiO_4$ were varied by the substitution of Zr for Ti. As Zr content was increased, the crystallinity of $KLaZr_xTi_{1-x}O_4$ was increased, which had a positive effect on the photocatalytic activity in the water splitting reaction. However, the direct band gap property was lost gradually with increase of Zr content, which resulted in lowering the photocatalytic activity. As a result, the highest activity was obtained for $KLaZr_{0.3}Ti_{0.7}O_4$. Although the absorption coefficients of photons for $KLaZr_{0.1}Ti_{0.9}O_4$ and $KLaTiO_4$ were higher than those for $KLaZr_{0.3}Ti_{0.7}O_4$, the crystal structure was disordered, which resulted in lowering the activity. The nickel-loaded catalysts showed a higher activity than unloaded perovskites by a factor of greater than 2.

KEY WORDS: $KLaTiO_4$; photocatalytic; water splitting; crystallinity; optical property.

1. Introduction

The photocatalytic decomposition of water into H_2 and O_2 has received special attention because of its potential for direct conversion of solar energy into chemical energy. Hydrogen (H_2) is an important chemical feedstock and is highly valued as a nonpolluting renewable fuel. Its production from cheap raw materials like water has been investigated enthusiastically. In a recent review, several new photocatalyst materials for overall water splitting were described [1]. Most of the active photocatalysts for water splitting have the perovskite-related structure such as $SrTiO_3$ [2], $Na_2Ti_6O_{13}$ [3], $K_4Nb_6O_{17}$ [4], $K_2Ti_4O_9$ [5], $BaTi_4O_9$ [6], $K_2La_2Ti_3O_{10}$ [7], and $La_2Ti_2O_7$ [8]. The relatively higher photocatalytic activity of these materials than that of the bulk-type simple oxides such as TiO_2 [9] and ZrO_2 [10] has been ascribed to their peculiar structure such as layered or tunnel structures.

Considering that $KLaTiO_4$ also has a layered perovskite structure, this material is also expected to have photocatalytic activity in water splitting reaction [11]. Photocatalytic activity of the layered perovkites is also highly dependent on the electronic band structure as well as the bulk crystal structure [12,13]. In particular, the shape of the valence and conduction band of a photocatalyst is greatly affected by the constituent elements, which would affect the electron-hole separation process after absorption of light with wavelengths shorter than its band gap energy. For the similar electronic band structures, the crystallinity of the solids is a critical variable that affects the photocatalytic activity [8].

In the present study, the effect of Zr substitution for Ti in $KLaTiO_4$ on the photocatalytic activity for water splitting will be discussed on the basis of the results by X-ray diffraction, UV-diffuse reflection spectra, BET surface area, and the energy dispersive analysis of X-ray (EDAX) analysis together with the electronic band structure calculation.

2. Experimental

Zr-substituted $KLaTiO_4$ ($KLaZr_xTi_{1-x}O_4$) was synthesized by a two-step ion-exchange reaction method [11]. At first, a series of $NaLaZr_xTi_{1-x}O_4$ ($x = 0$, 0.1, 0.3, 0.5, 0.7, and 1.0) was prepared by conventional solid state reactions; the stoichiometric amounts of La_2O_3 (Aldrich, 99.9%), ZrO_2 (Aldrich, 99.9%), and TiO_2 (Aldrich, anatase, 99.9%), and 20% excess Na_2CO_3 (Aldrich, 99.9%) were mixed and ground well in the presence of ethanol using a ball mill [14,15]. The ground mixtures were calcined at 1223 K for 30 min. $HLaZr_xTi_{1-x}O_4$ was formed by reaction of $NaLaZr_xTi_{1-x}O_4$ with 0.1 N HNO_3 at 25 °C for 24 h. Finally, $KLaZr_xTi_{1-x}O_4$ was synthesized by treatment of $HLaZr_xTi_{1-x}O_4$ (1 g) with 1 M KOH solution (100 mL) at 60 °C for 3 days, which was washed with distilled water, filtered, and then dried at 120 °C for 12 h.

2 wt% of nickel was loaded on these materials using $Ni(NO_3)_2 6H_2O$ (Aldrich, 99.9%) by a wet-impregnation

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method to increase the photocatalytic activity. The nickel-loaded catalysts were reduced by passing hydrogen into a Pyrex glass cell with a flow rate of 22 μmol/s at 773 K for 2 h, and then oxidized by air with a flow rate of 22 μmol/s at 473 K for 1 h.

The photocatalytic reaction was carried out in a closed gas circulation system. The catalyst (300 mg) was dispersed in distilled water (500 mL) by magnetic stirring and irradiated by a high-pressure Hg lamp (Ace Glass Inc., 450 W) equipped with an inner irradiation quartz reaction cell. The evolved gases were analyzed by an on-line gas chromatography (TCD, molecular sieve 5 Å column, Ar carrier gas).

The band gap energy of prepared catalysts was determined by a UV/VIS spectrometer (Shimadzu, UV 2401). The BET surface area was determined by N_2 gas adsorption at 77 K in a constant volume adsorption apparatus (Micrometrics, ASAP 2012). Energy dispersive analysis of X-ray was recorded by using field emission scanning electron microscopy (Joel, JSM-6330 F). The crystal structure of the sintered powder was determined by an X-ray diffractometer (Mac Science Co., M18XHF) with monochromated Cu Kα radiation at 40 kV and 200 mA with a scanning speed of 4 °/min in the 2θ range between 10 and 60 °.

The electronic band structure calculation was based on the FLAPW (Full Potential Linearized Augmented Plane Wave) method which uses the generalized gradient approximation (GGA), an improvement of the local spin density approximation (LSDA) within the density functional theory, known to be an efficient and accurate scheme for solving the many-electron problem of a crystal. The Wien97 package was used in this study [10]. The crystallographic parameters including lattice parameters and atomic positions were adopted from the literature for the calculation [16].

3. Results and discussion

The synthesis of single phases of NaLaZr$_x$Ti$_{1-x}$O$_4$ ($x = 0$, 0.1, 0.3, 0.5, 0.7, and 1.0) and HLaZr$_x$Ti$_{1-x}$O$_4$ was confirmed by the X-ray diffractions, where all diffraction lines were matched well with the reported ones [14,15]. The level of ion exchange of H$^+$ with K$^+$ in HLaZr$_x$Ti$_{1-x}$O$_4$ was investigated by EDAX as shown in table 1. For all compositions, the protons were confirmed to be completely replaced by K$^+$ within experimental error by reaction with hot (60 °C) aqueous KOH for 3 days and thus, it was concluded that the obtained powder had a stoichiometric composition expected from KLaZr$_{1-x}$Ti$_x$O$_4$.

Table 1
EDAX Data for KLaZr$_x$Ti$_{1-x}$O$_4$ ($x = 0$, 0.1, 0.3, 0.5, 0.7, and 1.0)

x	Compound	Elemental ratios			
		K	La	Zr	Ti
0.0	KLaTiO$_4$	0.98	0.96	–	1.02
0.1	KLaZr$_{0.1}$Ti$_{0.9}$O$_4$	0.96	1.01	0.12	0.88
0.3	KLaZr$_{0.3}$Ti$_{0.7}$O$_4$	1.02	0.98	0.31	0.69
0.5	KLaZr$_{0.5}$Ti$_{0.5}$O$_4$	0.99	1.02	0.51	0.49
0.7	KLaZr$_{0.7}$Ti$_{0.3}$O$_4$	0.96	1.01	0.72	0.28
1.0	KLaZrO$_4$	0.97	0.98	1.01	–

As shown in figure 1, the diffraction peaks of KLaTiO$_4$ were broadened significantly due to the formation of hydrates in a humidified atmosphere [11]. The overall shape of diffraction pattern of KLaTiO$_4$ was not changed by the substitution of Zr for Ti, which is indicative of no significant change of the crystal structure. However, when Zr content increased, the peak broadening was diminished gradually and only sharp peaks were observed for KLaZr$_{0.5}$TiO$_4$ and KLaZr$_{0.7}$Ti$_{0.3}$O$_4$.

Figure 2 shows the UV-diffuse reflectance spectra of KLaZr$_x$Ti$_{1-x}$O$_4$ ($x = 0$, 0.1, 0.3, 0.5, 0.7, and 1.0). KLaTiO$_4$ showed the longest absorption edge of about

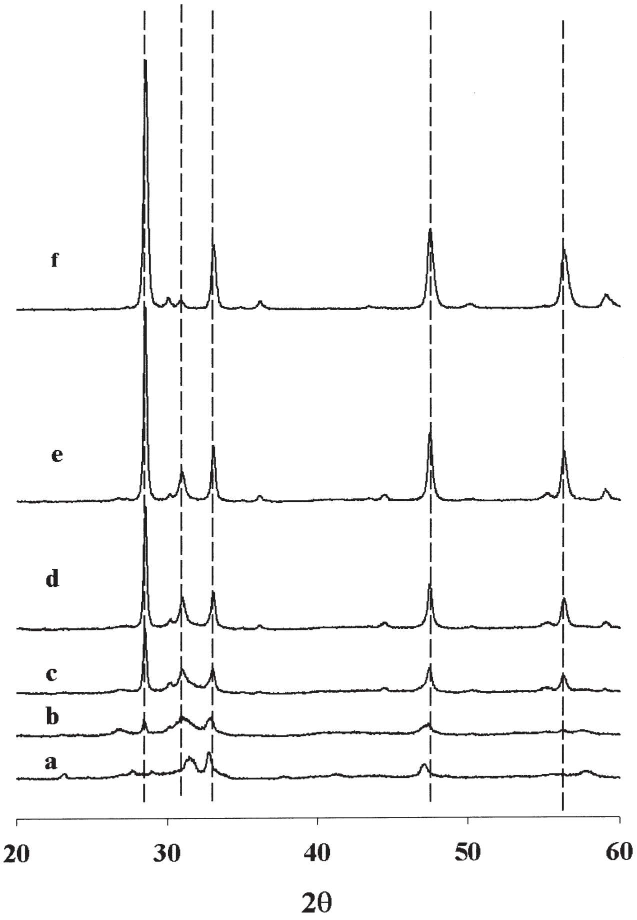

Figure 1. X-ray diffraction patterns of KLaZr$_x$Ti$_{1-x}$O$_4$ ($x = 0$, 0.1, 0.3, 0.5, 0.7, and 1.0). (a) $x = 0.0$ (KLaTiO$_4$), (b) $x = 0.1$ (KLaZr$_{0.1}$Ti$_{0.9}$O$_4$), (c) $x = 0.3$ (KLaZr$_{0.3}$Ti$_{0.7}$O$_4$), (d) $x = 0.5$ (KLaZr$_{0.5}$Ti$_{0.5}$O$_4$), (e) $x = 0.7$ (KLaZr$_{0.7}$Ti$_{0.3}$O$_4$), and (f) $x = 1.0$ (KLaZrO$_4$).

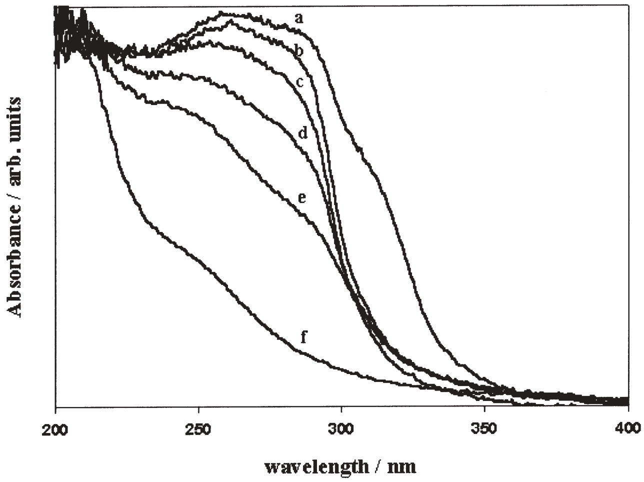

Figure 2. UV–Vis diffuse reflectance spectra of $KLaZr_xTi_{1-x}O_4$ ($x = 0$, 0.1, 0.3, 0.5, 0.7, and 1.0). (a) $x = 0.0$ (KLa TiO_4), (b) $x = 0.1$ ($KLaZr_{0.1}Ti_{0.9}O_4$), (c) $x = 0.3$ ($KLaZr_{0.3}Ti_{0.7}O_4$), (d) $x = 0.5$ ($KLaZr_{0.5}Ti_{0.5}O_4$), (e) $x = 0.7$ ($KLaZr_{0.7}Ti_{0.3}O_4$), and (f) $x = 1.0$ ($KLaZrO_4$).

345 nm. For $x = 0.1$ to 0.7, the absorption edges were blue-shifted to about 320 nm. It is noticeable that as Zr content increased up to $x = 0.7$, the absorption intensity was decreased with Zr content. For $KLaZrO_4$ ($x = 1.0$), the absorption edge was blue-shifted further to 280 nm.

The photocatalytic activities of $KLaZr_xTi_{1-x}O_4$ ($x = 0$, 0.1, 0.3, 0.5, 0.7, and 1.0) were measured and summarized together with the band gap energy and surface area in table 2. All the catalysts showed the photocatalytic activity in water splitting in a stoichiometric ratio and there was no indication of catalyst deactivation for 20 h, during which the catalyst had turned over many times making this overall water splitting a catalytic reaction. Nickel-loaded catalysts showed higher activities than unloaded ones by a factor of greater than 2. This increase in activity was due to its well-established role of nickel as a cocatalyst for perovskite-type photocatalysts [17]. Probably more remarkable is the fact that base materials exhibit high photocatalytic activities even without the promotional effect of nickel. This is unusual in photocatalytic water splitting over semiconductor photocatalysts. The photocatalytic activity was increased with Zr content up to $x = 0.3$, but after this composition, it was decreased with Zr content. Finally, $KLaTiO_4$ showed higher activity than $KLaZrO_4$ irrespective of the presence of nickel on its external surface. It is noticeable that the difference in surface area of these catalysts was not so significant, and thus the difference in photocatalytic activity was not ascribed to the difference in surface area. The photon flux from the UV lamp varies depending on the wavelength and, hence, the quantum yield is not necessarily proportional to the rate of H_2 production when semiconductors of different band gaps are used as catalysts. Thus, the quantum yields of H_2 evolution over photocatalysts were estimated to gauge the performance of each photocatalyst. The quantum yield is defined as the fraction of absorbed photons that is actually used to produce hydrogen or oxygen. It is the more meaningful parameter than the rate of H_2 evolution itself because the rate is normalized against the absorbed photons. The calibrated performance of these catalysts (quantum yield) is shown in figure 3. The band gap energy (3.59 eV) of $KLaTiO_4$ ($x = 0$) was the smallest, and thus it could absorb the largest number of photons (4100 μmol/h) to excite the electrons in the valence band. As Zr content was increased ($x = 0.1$–1.0), the band gap energy was increased with Zr content as shown in table 2, and thus the amount of photons that the photocatalyst could absorb was decreased. As a result, for $KLaZrO_4$, only about 2000 μmol/h of photons could be absorbed under the present irradiation condition. It is noticeable that the highest quantum yield of 12.5% was obtained for $x = 0.3$ ($KLaZr_{0.3}Ti_{0.7}O_4$) and $KLaTiO_4$ and $KLaZrO_4$ had the similar photocatalytic activity represented in the quantum yield. The quantum yield of 12.5% is not one of the highest known in the literature (e.g., 23% for $Sr_2Nb_2O_7$ [17] was reported). Yet, there are not many known photocatalysts that show quantum yields higher than 10%. More important, however, is the marked effect of Zr substitution on the photocatalytic activity of $KLaTiO_4$.

On the basis of the FLAPW method, which uses the GGA within the density functional theory (DFT), the electronic band structure of $KLaTiO_4$ and $KLaZrO_4$ were calculated. The crystallographic parameters including lattice parameters and atomic positions were adopted from the literature for the calculation [11]. According to this calculation, we found that the band gap energy of $KLaTiO_4$ and $KLaZrO_4$ is 2.2 eV and 3.7 eV respectively, as shown in figure 4. Although this calculation underestimates band gap energies especially for $KLaTiO_4$, it provides useful information on the nature of band structure. The conduction bands of $KLaTiO_4$ and $KLaZrO_4$ consist of empty Ti_3d and Zr_4d respectively, while the valence bands consist of occupied O_2p orbital for both materials. For the spectral energy close to the fundamental absorption edge ($E > E_g$), the dominant mechanism for optical absorption is the excitation of an electron from the valence band to the conduction band, which depends on the nature of electron transition mechanism (direct or indirect excitation).

The band gap of $KLaTiO_4$ with smallest band gap energy (3.59 eV) seems to be direct considering the sharp absorption onset, while that of $KLaZrO_4$ with largest band gap energy (4.42 eV) be indirect. Therefore, a direct optical transition can occur with no significant change of wave vector for $KLaTiO_4$. This direct band gap is one of the desirable properties of photocatalyst materials, since light absorption for this kind of materials can occur more efficiently compared with

Table 2
Photocatalytic decomposition of water over $KLaZr_xTi_{1-x}O_4$ with and without Ni loading along with their band gap energy and surface area

x	Band gap energy (eV)[a]	Surface area (m^2/g)	Activity without Ni loading ($\mu mol/g_{cat}.h$)[b]		Activity with Ni loading ($\mu mol/g_{cat}.h$)[b]	
			H_2	O_2	H_2	O_2
0.0	3.59	3.59	36	17.6	86	44
0.1	3.89	3.74	65.4	32.9	162	81
0.3	3.91	3.82	84.2	42.8	230	116
0.5	3.92	4.16	69.2	35.4	145	72
0.7	3.97	3.52	34	16.8	91	46
1.0	4.42	3.43	12.5	7.2	31	16

[a] Estimated from the adsorption edge of the diffuse reflectance spectra.

[b] Reaction condition: catalyst 300 mg, distilled water 500 mL, 450 W high-pressure Hg lamp, inner irradiation-type reaction cell made of quartz.

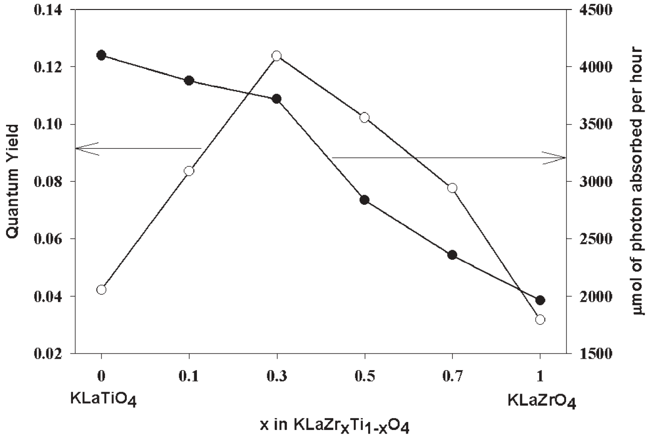

Figure 3. The quantum yield and the rate of photon absorption of $KLaZr_xTi_{1-x}O_4$ ($x = 0, 0.1, 0.3, 0.5, 0.7$, and 1.0). 2 wt% of nickel was loaded for all catalysts. The quantum yield was calculated using the following equation: Q.Y = 2× number of H_2 per number of photon absorbed by photocatalyst. The number of absorbed photons was determined by light flux meter (1815-C, Newport) with the light sensor attached to the photocatalytic reactor.

that for materials with the indirect band gap. With increase in Zr content in $KLaZr_xTi_{1-x}O_4$, this direct band gap property is decreased, as demonstrated by the reduction in the absorption coefficient in figure 2. Therefore, $KLaTiO_4$ should have the highest photocatalytic activity among all catalysts with the different compositions of Ti and Zr in $KLaZr_xTi_{1-x}O_4$. However, the highest quantum yield of 12.5% was obtained for

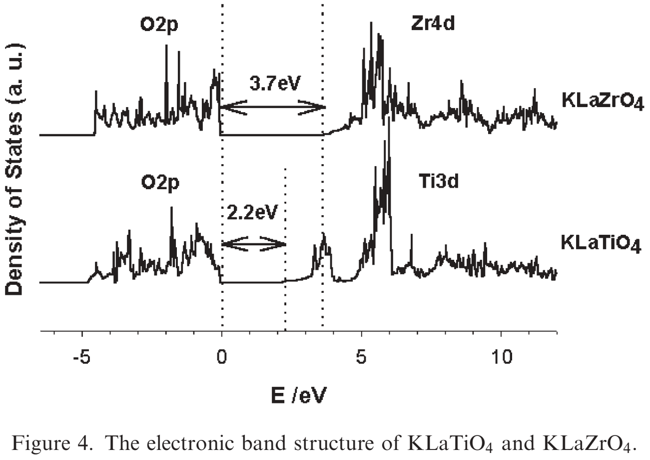

Figure 4. The electronic band structure of $KLaTiO_4$ and $KLaZrO_4$.

$x = 0.3$ ($KLaZr_{0.3}Ti_{0.7}O_4$) and $KLaTiO_4$ and $KLaZrO_4$ had the similar photocatalytic activity (quantum yield). The existence of the optimum composition that gave the highest activity was ascribed to the fact that an efficient photocatalyst should also have a high crystallinity as well as the desirable optical property because a defect in structure could provide a site for electron-hole recombination. As Zr content was increased, the crystallinity was increased as seen in figure 1. Therefore, there exists an optimum Zr content that gives maximum photocatalytic activity.

As a conclusion, both the optical property and the crystallinity of $KLaTiO_4$ were varied by the substitution of Zr for Ti. As Zr content was increased, the crystallinity of $KLaZr_xTi_{1-x}O_4$ was increased, which had a positive effect on the photocatalytic activity in a water splitting reaction. However, the direct band gap property was lost gradually with increase of Zr content, which resulted in lowering the photocatalytic activity. These factors gave an optimum Zr and Ti composition in $KLaZr_xTi_{1-x}O_4$.

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