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Photocatalytic effect and Mössbauer study of iron titanium silicate glass prepared by sol-gel method

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Abstract A relationship between the photocatalytic effect and the local structure of $50Fe_2O_3 \cdot (50-x)SiO_2 \cdot xTiO_2$ glass abbreviated as 50FSxTi prepared by sol-gel method was investigated by ^{57}Fe-Mössbauer spectroscopy (FeMS), X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FT-IR) and ultraviolet-visible diffuse reflectance spectroscopy (UV-VIS). Mössbauer spectra of 50FSxTi glass before annealing showed a doublet with the isomer shift (δ) and quadrupole splitting (Δ) of $0.41_{\pm 0.01}$ mm s^{-1} and $0.75_{\pm 0.02}$ mm s^{-1}, indicating that Fe^{3+} formed FeO_6 octahedra (O_h). A comparable δ of $0.36_{\pm 0.02}$ mm s^{-1} and the larger Δ of $0.92_{\pm 0.02}$ mm s^{-1} values were confirmed for 50FSxTi after annealed at 400 °C for 3 h. These results indicates that the coordination number of iron polyhedra decreases from 6 to 4 due to annealing. UV-VIS diffuse reflectance spectra of 50FS10Ti yielded two optical band gap energies (E_g's) of 2.05 eV and 3.55 eV. This result implied that 50FS10Ti has two optical band gaps in the visible area and UV area. A bleaching test performed by 10 mL of MB aqueous solution and 40 mg of powder 50FS10Ti glass sample showed that MB absorbance decreased from 3.16 to 0.43 after UV-visible light irradiation for 2 h with the first order rate constant (k) of 1.6×10^{-2} min^{-1}. These results prove that titanium containing iron silicate glass with the composition of $50Fe_2O_3 \cdot 40SiO_2 \cdot 10TiO_2$ has the UV and visible light responsive photocatalytic effect.

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1 Introduction

Since UV light assisted water decomposition into hydrogen and oxygen on anatase type TiO_2 electrodes was discovered in 1972 [1], photocatalysis by TiO_2 semiconductors has received much attention and been widely studied with the goal of converting solar energy into the useful chemical energy. Anatase type TiO_2 semiconductor photocatalysts have relatively large band gap of 3.2 eV, corresponding to wavelength shorter than 388 nm. This means that anatase type TiO_2 can use only 3 % – 4 % of the solar energy that reaches the earth's surface for UV light source for its use. In order to increase the efficiency, a lot of visible light activated photocatalysts containing anatase type TiO_2 have been investigated [2–7]. However, visible light activated photocatalysts other than TiO_2 are difficult to use practically, since they might need rare metals such as W, Ga, Au, Ta and Ge [8–13]. Thus, visible light activated photocatalysts without rare metals are extensively required for environmental purification.

Recently, Kubuki et al. reported that iron containing soda-lime silicate glass with the composition of $15Na_2O \bullet 15CaO \bullet 50Fe_2O_3 \bullet 20SiO_2$ prepared by conventional melt quenching method showed visible light activated photocatalytic effect with the first order rate constant (k) for methylene blue (MB) decomposition of 2.87×10^{-2} h^{-1} [14]. In our previous paper, heat-treated $50Fe_2O_3 \cdot 50SiO_2$ glass prepared by sol-gel method decomposed MB with the larger k of 6.48×10^{-2} h^{-1} under visible light irradiation [15].

In order to develop a photocatalyst with high efficiency, a relationship between the local structure and photocatalytic effect of $50Fe_2O_3 \cdot (50 - x)SiO_2 \cdot xTiO_2$ glass after annealing at 400 °C for 3 h prepared by sol-gel method was investigated by means of ^{57}Fe-Mössbauer spectroscopy (FeMS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and ultraviolet-visible spectroscopy (UV-VIS).

2 Experimental

Titanium containing iron silicate glass with a composition of $50Fe_2O_3 \cdot (50-x)SiO_2 \cdot xTiO_2$ ($x = 10 - 40$ mass %, abbreviated as 50FSxTi) was prepared by a sol-gel method. Reagent chemicals of $Si(OC_2H_5)_4$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ti(OCH(CH_3)_2)_4$, 7.8 M HNO_3 and C_2H_5OH were poured into a beaker and mixed well for 2 h at RT. After having been agitated by reflux-heat method at 80 °C for 2 h, the solution was poured into a glass vial and dried at 60 °C for 3 days to get a dark brown glass sample. The prepared glass was annealed at 400 °C for 3 h in air. For evaluation of the influence of titanium, $50Fe_2O_3 \cdot 50SiO_2$ (abbreviated as 50FS) was also prepared in the same method. ^{57}Fe-Mössbauer spectra were recorded at RT by a constant acceleration method. ^{57}Co(Rh) with the radioactivity of 925 MBq and α-Fe foil were used for a source and a reference, respectively. The obtained Mössbauer spectra were analyzed by Lorentzian fitting using Mösswinn 3.0i XP. XRD profiles were recorded at 2θ between 10° and 80° with an interval and scanning rate of 0.02° and 5° min^{-1}, respectively. X-rays with the wavelength (λ) of 1.54 Å were generated by Cu filament targeted by electron accelerated by 40 mA and 40 kV. FT-IR spectra were measured by KBr disk method between the wavenumber of 400 and 4000 cm^{-1} under the resolution of 2 cm^{-1}. To estimate the optical band gap of these glass samples, UV-VIS diffuse reflectance spectra with the

wavelength between 200 and 800 nm were recorded by using the UV-VIS spectrophotometer with the integrating sphere attachment. The obtained diffuse reflectance spectra were converted to Tauc Plots using the Kubelka-Munk function in order to estimate the optical band gap energy [16–19]. This conversion was carried out by means of UV-VIS control and analysis software (UVProve, Shimadzu). For evaluation of photocatalytic effect, 40 mg of well-pulverized annealed 50FSxTi glass was soaked into 10 mL of methylene blue aqueous solution (MB_{aq}) with the concentration of 33.3 μM (= 10.6 mg L^{-1}). Bleaching test was carried out for 2 h at RT using a glass vial irradiated with a visible light with the wavelength (λ) between 420 and 750 nm or the UV-visible light with λ between 380 and 750 nm. The range switching of the irradiation wavelength was carried out by attaching and detaching the UV-cutoff filter. Absorbance of MB_{aq} before and after the bleaching test was determined by UV-VIS absorption spectroscopy between the wavelength of 200 and 800 nm using a UV-VIS spectrophotometer.

3 Results and discussion

^{57}Fe-Mössbauer spectra of 50FSxTi glass with 'x' between 10 and 40 before and after annealing at 400 °C for 3 h are shown in Fig. 1. Before the annealing (Fig. 1a), all the spectra were composed of a paramagnetic doublet with a constant isomer shift (δ) and quadrupole splitting (Δ) are $0.41_{\pm 0.01}$ mm s^{-1} and $0.75_{\pm 0.02}$ mm s^{-1} due to $Fe^{III}O_6$ octahedra (O_h) [20]. In contrast, Mössbauer spectra of 50FSxTi glass with 'x' between 10 and 40 after isothermal annealing at 400 °C for 3 h (Fig. 1b) showed a paramagnetic doublet with δ of $0.36_{\pm 0.02}$ and Δ of $0.92_{\pm 0.02}$ mm s^{-1} due to $Fe^{III}O_4$ tetrahedra (T_d) [20]. It can be said that the titanium containing iron silicate glass can be successfully prepared by the annealing at 400 °C for 3 h, since coordination number of Fe^{3+} in the silicate glass matrix is four in most case according to the reference [20]. XRD profiles of 50FSxTi before and after annealing at 400 °C for 3 h are shown in Fig. 2. It is clear that obtained glass samples had amorphous structure since halo patterns were confirmed. These results show that iron ion in the 50FSxTi glass keeps amorphous Fe^{3+} state and composes glass matrices with silicon and titanium even though iron is not a typical network former (NWF) like silicon. FT-IR spectra of 50FSxTi glass with 'x' between 10 and 40 before and after annealing at 400 °C for 3 h are shown in Fig. 3. All spectra before annealing displayed two characteristic broad absorptions centered at 3480 and 1620 cm^{-1} which are ascribed to the stretching and bending modes of vibrations of water and hydroxyl group [21], and the intensity of these two broad absorptions decreased after annealing. Moreover, two characteristic absorptions at 786 and 690 cm^{-1} which are showing the stretching and bending modes of vibrations of silanol group (Si-OH) [22] and one strong absorption at 1384 cm^{-1} referring to the nitrate ion (NO_3^-) [21] before annealing, vanished after annealing. These results indicate that, nitrate ion and hydroxyl group connecting to silicon have disappeared due to annealing though the water remained in the glass matrices. From these results, it can be said that iron in the 50FSxTi changed from Fe^{3+} (O_h) to Fe^{3+} (T_d) by the annealing with the removal of NO_3^- and Si-OH.

UV-VIS diffuse reflectance spectra of 50FS and 50FSxTi glass with 'x' of 10, 20, 30 and 40 after annealing at 400 °C for 3 h are shown in Fig. 4. An absorption edge in visible light region with the wavelength of 500–700 nm can be observed for all the spectra. It should be noted that a new optical band gap corresponding to ultraviolet light area with the wavelength of 300–360 nm was confirmed only for annealed 50FS10Ti glass. From the Tauc plots of these samples in Fig. 5, the optical band gaps of 50FS and 50FSxTi with x of 10, 20, 30 and

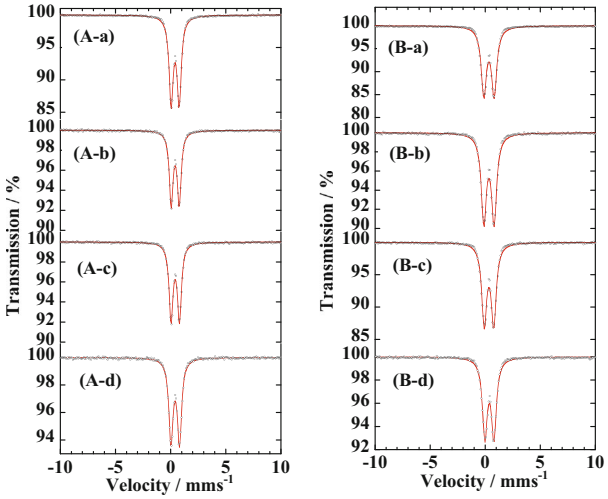

Fig. 1 ^{57}Fe-Mössbauer spectra of 50FSxTi glass with 'x' of **a** 10, **b** 20, **c** 30 and **d** 40 measured **A** before and **B** after annealing at 400 °C for 3 h

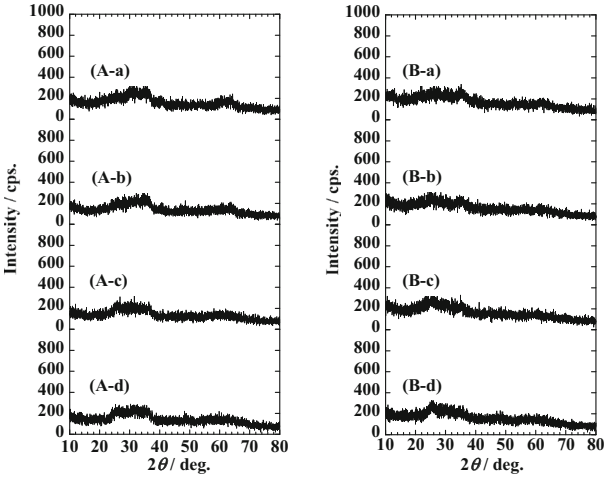

Fig. 2 XRD profiles of 50FSxTi glass with 'x' of **a** 10, **b** 20, **c** 30 and **d** 40 measured **A** before and **B** after annealing at 400 °C for 3 h

40 in the visible light area were estimated to be 2.01 eV, 2.05 eV, 1.91 eV, 2.05 eV and 2.08 eV, respectively. Moreover, a new band gap formed in 50FS10Ti was calculated to be 3.55 eV which corresponds to UV light region. These results show that 50FS10Ti might have both UV and visible light responsiveness in the photocatalytic reaction since 50FS10Ti has the two different optical band gaps.

As shown in Fig. 6, absorbance of 10 mL MB_{aq} bleached with 40 mg of annealed 50FS and 50FSxTi glass with 'x' between 10 and 40 were plotted against bleaching time. In addition, k values for MB decomposition in the bleaching test are indicated in Fig. 7. Considering the condition under visible light irradiation, it can be said that 50FS which has the largest k's value of 1.06×10^{-2} min^{-1} has high photocatalytic effect. However, the absorbance of 0.43 in case using annealed 50FS10Ti under the UV-visible light irradiation is obviously lowest in all conditions and in all samples after 2 h bleaching (Fig. 6

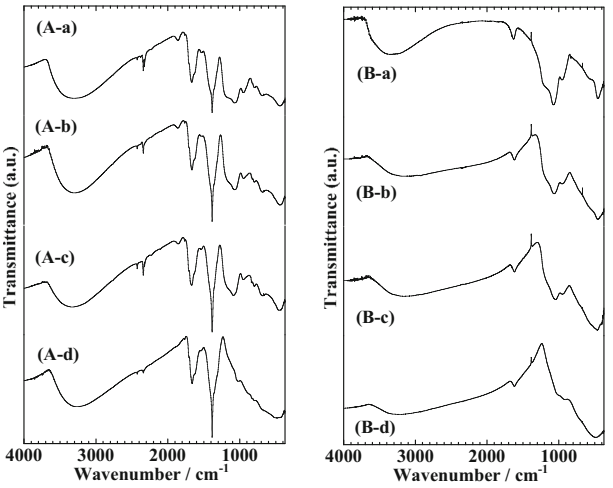

Fig. 3 FT-IR spectra of 50FS*x*Ti glass with '*x*' of **a** 10, **b** 20, **c** 30 and **d** 40 measured **A** before and **B** after annealing at 400 °C for 3 h

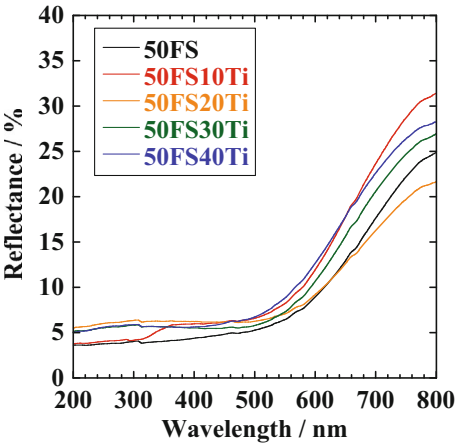

Fig. 4 UV-Vis diffuse reflectance spectra of (*black*) 50FS and 50FS*x*Ti glass with '*x*' of (*red*) 10, (*orange*) 20, (*green*) 30 and (*blue*) 40 measured after annealing at 400 °C for 3 h

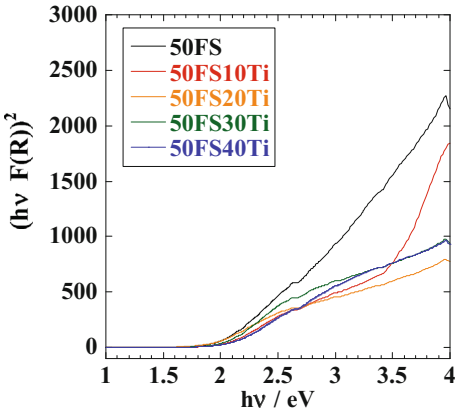

Fig. 5 Tauc plot of (*black*) 50FS and 50FS*x*Ti glass with '*x*' of (*red*) 10, (*orange*) 20, (*green*) 30 and (*blue*) 40 measured after annealing at 400 °C for 3 h

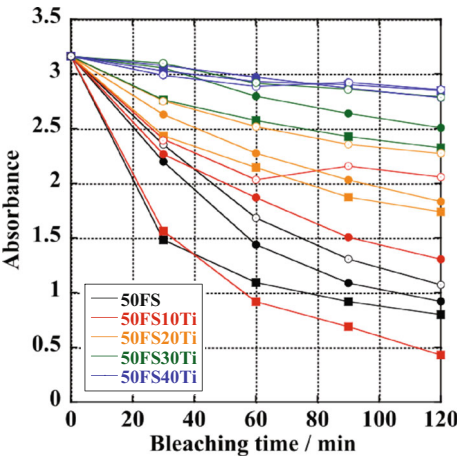

Fig. 6 Absorbance *vs.* t plot in bleaching test using 10 mL MB_{aq} and 40 mg of annealed (*black*) 50FS and 50FSxTi glass with 'x' of (*red*) 10, (*orange*) 20, (*green*) 30 and (*blue*) 40. Opened circle, closed circle and closed square showed in case of dark, under the visible light irradiation and under the UV-visible light irradiation, respectively

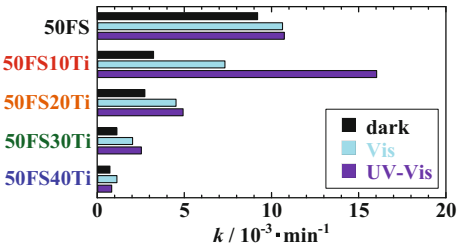

Fig. 7 First order rate constant (k) of the bleaching test using annealed 50FS and 50FSxTi glass with 'x' of 10, 20, 30 and 40. The *black*, *blue* and *violet* bar showed k values estimated in the dark, under the visible light and under the UV-visible light, respectively

red square). Moreover, all samples except for 50FS10Ti have no clear difference in the absorbance under the visible light irradiation and that under the UV-visible light irradiation. These results show that annealed 50FS10Ti exhibited photocatalytic effect not only under visible light irradiation but also under UV-visible light irradiation. It is concluded that annealed 50FS10Ti glass has the practical photocatalytic effect which is responsive to both visible and UV lights.

4 Summary

A relationship between the structure and photocatalytic effect of $50Fe_2O_3 \cdot (50 - x)SiO_2 \cdot xTiO_2$ (x = 10–40 mass %, abbreviated as 50FSxTi) glass after isothermal annealing was investigated by ^{57}Fe-Mössbauer spectroscopy, X-ray diffractometry, Fourier transform infrared spectroscopy and UV-vis spectroscopy. After isothermal annealing at 400 ° C for 3 h, 50FSxTi glass with 'x' of 10 to 40 remained an amorphous structure and Fe^{3+} (O_h) in 50FSxTi glass before annealing was turned to Fe^{3+} (T_d) with the removal of the nitrate ion and hydroxyl group connecting to silicon. From the UV-Vis diffuse reflectance spectra, two optical band gaps with the energy of 2.05 eV and 3.55 eV were estimated for annealed 50FS10Ti. Bleaching test using methylene blue aqueous solution (MB_{aq}) and annealed 50FS10Ti glass showed the largest first order rate constant (k) of 1.60×10^{-2} min^{-1} under UV-visible light irradiation. In contrast, k value under the visible light irradiation was 7.3×10^{-3} min^{-1}. It is concluded that new optical band gap formed in 50FS10Ti glass

after annealing can be controlled by changing $Fe_2O_3/SiO_2/TiO_2$ ratio, and that UV and visible light responsive photocatalytic effect appears since the band gap in UV area was newly formed. This newly developed titanium containing iron silicate glass can be utilized for environmental purifications under the sun light.

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