Characterization of Ti-doped CaFe$_2$O$_4$ prepared from a malic acid complex

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Ti-doped and undoped CaFe$_2$O$_4$ powders were prepared from a malic acid complex and their properties were evaluated using analytical instruments. According to an XRD measurement, there were no traces of impurity phases in 5 mol % Ti-doped CaFe$_2$O$_4$ powder, while impurity phases such as $\alpha$-Fe$_2$O$_3$ and CaTiO$_3$ were observed for 10 mol % Ti-doped CaFe$_2$O$_4$. When Ti was added to CaFe$_2$O$_4$, the crystallite growth of CaFe$_2$O$_4$ was suppressed and the BET surface area increased. SEM observation revealed that the addition of Ti atoms to CaFe$_2$O$_4$ causes interconnected CaFe$_2$O$_4$ particles to separate. From the results of an XRF measurement, it is suggested that Fe atoms are substituted with Ti atoms. The optical band gap of CaFe$_2$O$_4$ hardly changed as a result of doping with Ti.

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For several decades, the physical and chemical properties of calcium ferrite (CaFe$_2$O$_4$) crystal have been researched widely because of its useful applications such as in gas absorbers, in electrochemical devices for high-temperature use, and as an oxidation catalyst.\(^{1-3}\) CaFe$_2$O$_4$ has recently attracted considerable attention as a new photocatalyst material owing to its excellent photoelectroductive property for H$_2$O and CO$_2$.\(^{4,5}\) In general, CaFe$_2$O$_4$ is prepared by a solid-state reaction. Although a solid-state reaction is most frequently used because of easy and convenience, it has several problems such as changes in stoichiometric ratio and the ease of formation of impurity phases.\(^{6,7}\) This is because the starting materials must be repeatedly ground and calcined many times to prepare the intended crystal phase. As a result, the specific surface area of the product decreases and the catalytic activity has inevitably falls. Needless to say, a high surface area is an important property of surface functionality materials such as catalysts.

Marecilly and co-workers have reported a new preparation method employing organic acids (citric, malic, tartaric, glycolic acids etc.) to obtain metal oxides.\(^{11}\) They showed that H$^+$ in an organic acid with -OH or -COOH groups is replaced by the metal ion in the solution and the organic acid complex is easily formed. This complex is available for a precursor to prepare the intended material. Therefore, it is expected that the precursor is transformed to objective oxide at lower calcination temperature than the case of a solid-state reaction method and the resulting final product has a large surface area and a high homogeneity.

In the present study, we have examined the preparation of CaFe$_2$O$_4$ powder with high specific surface area from a malic acid complex, instead of employing a solid-state reaction, and characterized the powder by X-ray diffractometry (XRD), X-ray photoelectron spectrometry (XPS), fluorescence X-ray spectrometry (XRF), scanning electron microscopy (SEM), surface area measurement, and UV–vis spectrometry. Furthermore, the effect of Ti addition on the crystal phase, microstructure, specific surface area, and optical properties of CaFe$_2$O$_4$ was investigated.

CaFe$_2$O$_4$ powder was synthesized by a malic acid complex method. Ca(NO$_3$)$_2$·4H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and malic acid in a 1:2:3 molar ratio were dissolved in deionized water. The addition of Ti to CaFe$_2$O$_4$ carried out using Ti[OCH(CH$_3$)$_2$]$_4$. The amount of Ti doped set to 5 and 10 mol % to Fe. The solution was dehydrated and heated on a hot plate to prepare the precursor powder of CaFe$_2$O$_4$. Then, the precursor was calcined in the temperature range of 700 to 900°C in air for 12 h. On the other hand, CaCO$_3$ and $\alpha$-Fe$_2$O$_3$ as the starting materials were mixed in a 1:2 molar ratio in a solid-state reaction. The mixture was also calcined at 700, 800, and 900°C in air for 12 h. The heating ratio was set to 10°C/min in all cases. Powder X-ray diffraction (XRD) measurement was carried out to analyze the crystal structure of the calcined powder. XRD patterns were recorded by Cu-K$_\alpha$ radiation under the following conditions: sweep rate: 2°/min and 30 kV–20 mA. PDF files were used to identify the crystal phases.\(^{12}\) Chemical composition and bonding state of the heat-treated precursor was checked by X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence (XRF) measurement. The specific surface area of the powder was measured from the adsorption isotherm of N$_2$ at $-196^\circ$C by the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.1 < $p/p_0$ < 0.3.\(^{13}\) The microstructural observation of the sample was performed by scanning electron microscopy (SEM). The diffuse reflectance spectrum (DRS) was collected by a UV–vis spectrometer in the wavelength of 400 to 800 nm at room temperature.

**Figures** 1(a) and 1(b) show XRD patterns of the sample powders prepared from a malic acid complex and by a solid-state
reaction, respectively. For the former powder, almost all of the diffraction peaks at 700°C can be ascribed to the CaFe$_2$O$_4$ phase and the lattice parameters were calculated to be $a = 0.92281$, $b = 1.07050$, and $c = 0.30185$ nm, which are in good agreement with the reference values (PDF 00-032-0168). In contrast, a mixture phase consisting of CaCO$_3$, Ca$_2$Fe$_2$O$_5$, and $\alpha$-Fe$_2$O$_3$ was confirmed at 800°C or below in the powder prepared by the solid-state reaction. When the mixture was heated to 900°C, these impurities almost disappeared and a CaFe$_2$O$_4$ phase with high purity appeared. From the comparison between Figs. 1(a) and 1(b), it is clear that the temperature at which the CaFe$_2$O$_4$ phase with high purity was formed when using the malic acid complex was at least 100°C lower than that when the solid-state reaction was employed.

Figure 2 depicts the XRD patterns of the Ti-doped CaFe$_2$O$_4$ powders prepared from the malic acid complex. There were no traces of impurity phases in the 5 mol% Ti-doped CaFe$_2$O$_4$ powder. This suggests that the solubility limit of Ti atoms in CaFe$_2$O$_4$ is above 5 mol%. For 10 mol% Ti-doped CaFe$_2$O$_4$ powder, the mixture phase consisting of $\alpha$-Fe$_2$O$_3$, CaTiO$_3$, and CaFe$_2$O$_4$ was confirmed. Figure 3 shows the relationship between the lattice parameters ($a$, $b$, and $c$) of CaFe$_2$O$_4$ and the amount of Ti additives. Parameter $a$ increased when 5 mol% Ti was added but decreased when 10 mol% Ti was added. Parameter $b$ rose monotonically until 10 mol% Ti addition, while parameter $c$ hardly changed when 5 mol% Ti was added and decreased when 10 mol% Ti was added.

Figure 4 shows XPS spectra of Ca 2p, Fe 2p, O 1s, and Ti 2p for 5 mol% Ti-doped CaFe$_2$O$_4$ powder in comparison with those for undoped CaFe$_2$O$_4$ powder. A charge correction was made by considering that the C 1s signal was centered at 285.0 eV. In the O 1s signal, there are two components at around 529.5 and 531.4 eV. The former corresponds to lattice oxygen and the latter corresponds to carbonate formed at the surface of CaFe$_2$O$_4$. The binding energies of the Ca 2p and Fe 2p signals are in good agreement with those of the Ca$^{2+}$ and Fe$^{3+}$ valence states. Also, satellite peaks of Fe 2p were observed in the range of 716.0 to 721.0 eV, indicating that Fe$^{3+}$ is dominant in both samples. Although the charge compensation of incorporated Ti$^{4+}$ increase...
via the reduction of additional Fe$^{3+}$ to Fe$^{2+}$ species, it is difficult to clearly distinguish Fe$^{2+}$ from Fe$^{3+}$ as shown in Fig. 4. In addition, it is not easy to separate the Ti 2p spectrum from the background. Therefore, an XRF measurement was carried out for Ti-doped CaFe$_2$O$_4$, the results of which are shown in Fig. 5.

A peak of Ti-K$_x$ was observed at 4.5 keV for the mixture of CaFe$_2$O$_4$ and TiO$_2$, similar result was also obtained for 10 mol\% Ti-doped CaFe$_2$O$_4$. In contrast, the Ti-K$_x$ peak of 5 mol\% Ti-doped CaFe$_2$O$_4$ appeared at a different position from that of 10 mol\% Ti-doped CaFe$_2$O$_4$, suggesting that the Fe atoms are substituted with Ti atoms.

Table 1 summarizes the mean crystallite size and specific surface area for Ti-doped and undoped CaFe$_2$O$_4$ powders prepared from a malic acid complex. The mean crystallite size of the samples was estimated from the full width at half maximum (FWHM) of the (112) diffraction peak at 2$\theta$ = 33.5$^\circ$ using Scherrer’s equation. After calcination at 700°C in air for 12 h, the crystallite sizes were estimated to be 49.7, 47.2, and 44.6 nm for undoped, 5 mol\% Ti-doped, and 10 mol\% Ti-doped CaFe$_2$O$_4$, respectively. Although the crystallite size of the Ti-doped and undoped CaFe$_2$O$_4$ increased with increasing calcination temperature, the crystallite growth of CaFe$_2$O$_4$ appeared to be suppressed by adding Ti. The specific surface area of the undoped CaFe$_2$O$_4$ powder was calculated to be 8.0 m$^2$/g after calcination at 700°C in air for 12 h, by applying the least-squares method to its BET plot. When Ti was added to CaFe$_2$O$_4$, the BET surface area gradually increased with increasing amount of Ti. On the other hand, in the case of the solid-state reaction, the powder calcined at 900°C for 12 h had a low value (1.7 m$^2$/g), which is much smaller than the value obtained using the malic acid complex.

In order to investigate the morphology and microstructure of Ti-doped and undoped CaFe$_2$O$_4$ powders, SEM observation was carried out. Figure 6 presents SEM photographs of the Ti-doped and undoped powders calcined at 700°C for 12 h in air. Undoped CaFe$_2$O$_4$ powder consists of tightly interconnected grains with a primary particle size in the range of 0.2–0.4 μm. Also, each grain has an irregular shape. When 5 mol\% Ti was added to CaFe$_2$O$_4$, the opening volume between the primary particles increased. For 10 mol\% Ti-doped CaFe$_2$O$_4$, many fine particles were clearly observed. The change in the microstructure as seen in the SEM images shows that Ti-doped CaFe$_2$O$_4$ powder has a larger specific surface area than undoped CaFe$_2$O$_4$ powder, as expected from the results of BET measurement.

The UV–vis DRS for the precursor calcined at 700°C in air for 12 h were collected in the wavelength range of 400 to 800 nm at room temperature. Figure 7 shows spectral dependence of the Kubelka–Munk (KM) function defined by $f(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$, where $R_{\infty}$ is the diffuse reflectance of the CaFe$_2$O$_4$ powder prepared from a malic acid complex. The KM function $f(R_{\infty})$ for the semi-infinite case is given by $f(R_{\infty}) = \alpha / S$, where $\alpha$ and $S$ are the absorption coefficient and the scattering coefficient of powder, respectively. The absorption coefficient, $\alpha$, was determined by.\(^{17}\)

![Fig. 4. XPS spectra of O 1s, Ca 2p, Fe 2p, and Ti 2p for 5 mol\% Ti-doped and undoped CaFe$_2$O$_4$.](image)

![Fig. 5. XRF spectra for Ti-doped CaFe$_2$O$_4$ and a mixture of CaFe$_2$O$_4$ and TiO$_2$.](image)

![Table 1. Mean crystallite size and specific surface area for Ti-doped and undoped CaFe$_2$O$_4$ powder prepared from a malic acid complex](table)
where $A$, $h\nu$ and $E_g$ are a constant, the photon energy and the optical band gap, respectively. In this equation, $n$ depends on the nature of band transition, $n = 1/2$ for direct and $n = 2$ for indirect allowed transitions. For the CaFe$_2$O$_4$ powder calcined at 700°C, $n$ was estimated to be 1/2 from the slope of $ln R_{\omega}(\omega \nu) \nu$ vs. $ln (h\nu – E_g)$ plot, suggesting that CaFe$_2$O$_4$ is a direct-gap material. This result is not consistent with the theoretical results based on a GGA+$U$ calculation. This is because that the energy difference between the direct and indirect transition is very small as predicted by the GGA+$U$ approach. In addition, the optical band gap of undoped, 5, and 10 mol% Ti-doped CaFe$_2$O$_4$ powder were approximately estimated to be 1.9, 1.9, and 2.0 eV from the relation of $\{\{R_{\omega}(\omega \nu)\nu\}\nu\}$ vs. $h\nu$ plot, respectively.

A pure phase of CaFe$_2$O$_4$ appears at lower temperature in a malic acid complex method than in a solid-state reaction. There were no traces of impurity crystal phase in 5 mol% Ti-doped CaFe$_2$O$_4$, while impurity phase such as $\alpha$-Fe$_2$O$_3$ was observed for 10 mol% Ti-doped CaFe$_2$O$_4$. The specific surface area of CaFe$_2$O$_4$ powder increased with increasing the amount of Ti-doping. From the SEM observation, it was revealed that the addition of Ti atoms to CaFe$_2$O$_4$ has an effect to separate between tightly connective particles. The DRS measurement suggests that CaFe$_2$O$_4$ is an indirect-gap material and the optical band gap is estimated to be 1.9, 1.9 and 2.0 eV for undoped, 5 mol% Ti, and 10 mol% doped CaFe$_2$O$_4$, respectively.

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