Preparation of magnesium ferrite by a malic acid complex

Akane DOI,* Shigenori MATSUSHIMA,*** Kenji OBATA,*** Ryosuke MAEDA,** Atsushi KAJIMA** and Kenkichiro KOBAYASHI***

¹Department of Biological Functions and Engineering, Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology (KIT), Kitakyushu Science and Research Park, 2–4 Hibikino, Wakamatsu-ku, Kitakyushu 808–0196, Japan
²Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology (KCT), 5–20–1 Shii, Kokuraminami-ku, Kitakyushu 802–0985, Japan
³Department of Electrical and Electronic Engineering, Kitakyushu National College of Technology (KCT), 5–20–1 Shii, Kokuraminami-ku, Kitakyushu 802–0985, Japan
⁴Department of Materials Science and Chemical Engineering, Graduate School of Engineering, Shizuoka University, 3–5–1 Johoku, Hamamatsu 432–8011, Japan

Nanopowder of MgFe2O4 was prepared from an organic acid complex method. Among three kinds of organic acids examined, it was found from an XRD measurement that the highest purity powder of MgFe2O4 was obtained from a malic acid complex. SEM observation revealed that the powder is fluffy aggregates and each particle has irregular shape. The TG–DTA and IR measurements show that thermolysis process of a malic acid complex in air was mainly constructed at two stages consisting of dehydration and ligand pyrolysis. Furthermore, it was confirmed from a VSM measurement that the saturation magnetization of MgFe2O4 nanopowder is much smaller value than that of the bulk material.

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There has been a considerable interest in magnesium ferrite (MgFe2O4) owing to their useful properties such as catalyst, gas sensor, microwave device, fuel cell, drug delivery, and so forth.¹⁻⁷ In recent research, Mg ferrite has attracted attention as a photocatalyst because of smaller band gap energy than that of TiO2 with anatase-type structure.⁸ In the present study, we have examined to prepare nanosized MgFe2O4 powder without impurity by utilizing a malic acid complex. Then, the detailed characterization of obtained powder was carried out by thermal gravimetric-differential thermal analysis (TG–DTA), Fourier transform infrared (FTIR) spectroscopy, X-ray diffactometry (XRD), scanning electron microscopy (SEM), specific surface area measurement, and vibrating sample magnetometry (VSM).

MgFe2O4 powder was prepared from an organic acid complex method. Mg(NO3)2·4H2O, Fe(NO3)3·9H2O, and organic acid (malic acid, citric acid, or malonic acid) in a 1:2:3 molar ratio were dissolved in deionized water. The solution was dehydrated and heated on a hot plate to prepare the precursor powder of MgFe2O4. Then, the precursor was calcined in the temperature range of 400 to 900°C in air for 2 h. On the other hand, MgO and α-Fe2O3 as the starting materials were mixed with 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 2 h. The heating ratio was set to 10°C/min in all cases. The thermal decomposition of precursor powder was analyzed by TG–DTA measurement under a static atmosphere and FTIR spectrometry performed in the range of 400 to 4000 cm⁻¹. Powder X-ray diffraction (XRD) measurement was carried out to identify the crystal structure of prepared powder. XRD patterns were recorded with Cu-Kα radiation, sweep rate: 2°/min and 30kV–20mA. The PDF files were used to identify the crystal phases. The specific surface area of the powder was measured from the adsorption isotherm of N2 at −196°C by the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.1 < p/p0 < 0.3.¹⁷ The microstructural observation of the sample was performed by SEM and the magnetic property was measured by VSM at room temperature.

Figure 1 shows the result of TG–DTA analysis for the as-prepared precursor powder. The TG–DTA measurement carried out in ambient air at a heating rate of 10°C/min. The first weight decrease was observed in the temperature range of 50 to 280°C, resulting from desorption of water contained in the sample. The second weight decrease causing an exothermal decomposition

¹ Corresponding author: S. Matsushima; E-mail: smatsu@kct.ac.jp
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of the organic ligands, starting abruptly at about 280°C, was observed, followed by a long plateau above 420°C. The total weight loss agrees with the theoretical loss, calculated for the formation of MgFe₂O₄ from the precursor. These assignments are also supported from IR spectra as mentioned below.

Figure 2 depicts IR spectra for precursor powders heated on a hot plate (as-prepared) and at 400°C in air. For the as-prepared sample, an absorption band at around 3400 cm⁻¹ corresponds to the presence of OH group. The bands at 1657 and 1325 cm⁻¹ can be ascribed to stretching vibration of carboxyl group. In addition, the band at 1657 cm⁻¹ also includes bending vibration of OH group. These absorption spectra disappeared when the as-prepared precursor was heated at 400°C. The band at 2343 cm⁻¹ is ascribed to CO₂.18) Alternatively, the absorption at around 600 and around 450 cm⁻¹ are assigned to the vibration mode of M-O (M=Mg, Fe) bands in tetrahedral and octahedral sites, respectively, which is indicative of formation of MgFe₂O₄ structure.19)

Figures 3(a) and 3(b) show the XRD patterns of sample powders prepared from a malic acid complex and a solid-state reaction, respectively. In a malic acid complex method, some diffraction peaks were observed even for precursor powder heated on a hot plate. All the peaks can be ascribed to MgFe₂O₄ phase in comparison with a PDF file (PDF: 01-074-8054). When the precursor powder was calcined in the temperature range of 400 to 900°C in air, the diffraction peaks of MgFe₂O₄ became gradually large and sharp with the increase of calcination temperature. There were no traces of impurity phases in each diffraction pattern. The lattice parameter of MgFe₂O₄ obtained at 400°C was calculated to be a = 0.8373 nm, which is also good agreement with the reference value (PDF 01-074-8054).

The lattice parameter did not almost change with the decomposition temperature. In contrast, a mixture phase consisting of MgFe₂O₄, MgO, and α-Fe₂O₃ was confirmed in a solid-state reaction method even after the calcination at 1000°C, although the amount of MgO and α-Fe₂O₃ decreased as the heating temperature increased.

Figures 4(a) and 4(b) show XRD patterns of precursor powders prepared from a citric acid complex and a malonic acid complex. For both precursor powders, diffraction peaks of MgFe₂O₄ were observed even after the heating on a hot plate as well as a malic acid complex. However, small diffraction peaks of α-Fe₂O₃ appeared as previously reported.13) When these precursors were calcined in the temperature range of 400 to 900°C in air. At last, the α-Fe₂O₃ phase in both cases disappeared by heating to 1000°C, leading to the larger particle size and smaller specific surface area than in a malic acid complex. Thus, it is apparent from the comparison between Figs. 3 and 4 that fine powder of MgFe₂O₄ which does not include impurities is provided only for a malic acid. In general, thermal decomposition
of an organic acid complex in air consists of four steps, which are (1) dehydration, (2) ligand pyrolysis, (3) carbonation, and (4) metal oxide formation.\textsuperscript{20} However, the thermolysis behavior obtained from the TG–DTA and IR measurements was similar each other for the three kinds of organic acid complexes examined. Therefore, it is unclear about the reason why impurity phase was not formed only for malic acid at the present stage.

Figure 5 depicts the relationship between the mean crystallite size of MgFe\textsubscript{2}O\textsubscript{4} and decomposition temperature of precursor powder obtained from a malic acid complex. The crystallite size of MgFe\textsubscript{2}O\textsubscript{4} was evaluated from Williamson-Hall analysis.\textsuperscript{21} The value was estimated to be 5.7 nm for the precursor heated at 400°C for 2 h and then became large with elevating the decomposition temperature as shown in Fig. 5.

In order to investigate the morphology and microstructure of MgFe\textsubscript{2}O\textsubscript{4} powder, SEM observation was carried out. Figure 6 presents SEM photographs for MgFe\textsubscript{2}O\textsubscript{4} powders prepared from a malic acid complex and a solid-state reaction. The former was calcined at 400°C and the latter at 1000°C. For a malic acid complex, MgFe\textsubscript{2}O\textsubscript{4} powder consists of fluffy aggregates and the primary particle size is below 63 nm. Also, the morphology of each aggregate is irregular shape. On the other hand, many large particles above 160 nm were clearly observed in a solid-state reaction. The difference in microstructure suggests that MgFe\textsubscript{2}O\textsubscript{4} powder obtained from a malic acid complex has a larger specific surface area than that of MgFe\textsubscript{2}O\textsubscript{4} powder obtained from a solid-state reaction. In fact, the specific surface area of MgFe\textsubscript{2}O\textsubscript{4} powder was calculated to be 86.5 m\textsuperscript{2}/g after calcination at 400°C in air for 2 h, by applying the least squares method to BET plot.

Figure 7 depicts magnetic hysteresis curve of MgFe\textsubscript{2}O\textsubscript{4} powder in the temperature range of 400 to 800°C in air. These loops are typical for a soft magnetic material. The saturation magnetization (Ms) of MgFe\textsubscript{2}O\textsubscript{4} powder heated at 400°C for 2 h is evaluated to be 8.6 emu/g, which is much smaller value than that of the bulk material.\textsuperscript{22} The main reasons arise from surface disorder, cation distribution, defects, and superparamagnetic behavior of the ultrafine particles.\textsuperscript{23} As shown in Fig. 8, the Ms of MgFe\textsubscript{2}O\textsubscript{4} powder rose with increasing the crystallite size, suggesting the improvement of crystallinity and the decrease of lattice defect.
Among three kinds of organic acids examined, MgFe₂O₄ nanopowder without any impurity was prepared only from a malic acid complex. The TG-DTA and IR measurements show that thermolysis process of a malic acid complex in air was mainly constructed at two stages consisting of dehydration and ligand pyrolysis. In the XRD measurement, the mean crystallite size was estimated to be 5.7 nm for the sample heated at 400°C and then became large with elevating the decomposition temperature. From the SEM observation, it was revealed that the powder is fluffy aggregates and each particle has irregular shape. The VSM measurement showed that the saturation magnetization of MgFe₂O₄ nanopowder is much smaller value than that of the bulk material.

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