Morphology, microstructure, and surface area of La-added MgFe$_2$O$_4$ powder

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La-added and pure MgFe$_2$O$_4$ powders were prepared from a malic acid complex, and the effect of La-adding on the microstructure and specific surface area of MgFe$_2$O$_4$ powder were examined. There were no traces of impurity phases for pure MgFe$_2$O$_4$ powder in the X-ray diffraction measurement after calcination in the range of 600 to 800°C. When La atoms were added to MgFe$_2$O$_4$, the crystallite growth of MgFe$_2$O$_4$ was suppressed remarkably, resulting in a higher specific surface area in comparison with the pure material, and the lattice volume increased. X-ray photoelectron spectroscopy measurements showed that the binding energies of Mg 2s, Fe 2p, O 1s, and La 3d signals were in good agreement with the Mg$^{2+}$, Fe$^{3+}$, O$^{2-}$, and La$^{3+}$ valence states, respectively. Scanning electron microscopy observations revealed that MgFe$_2$O$_4$ powder shows an aggregation of granular particles and that the individual particles are tightly interconnected with each other, whereas smaller particles compared with pure MgFe$_2$O$_4$ were observed for the La-added powder. It was found from the N$_2$ adsorption measurement, moreover, that the amount of mesopore increases with La addition.

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1. Introduction

Preparation of finer particles with high purity and large specific surface areas is indispensable for the development of surface-functionalized ceramic materials with high performance. To date, MgFe$_2$O$_4$ nanopowder has been applied to CO oxidation catalysts, SO$_2$ absorbents, and chemical gas sensors. In a previous paper, we reported that MgFe$_2$O$_4$ nanopowder with high purity was obtained from organic acid complexes (citric, malic, and malonic acids). It attracted particular attention that MgFe$_2$O$_4$ nanopowder without impurities was prepared from only a malic acid complex and that the α-Fe$_2$O$_3$ phase appeared in other organic acids. The crystallite size of MgFe$_2$O$_4$ powder increased largely, however, by calcining at higher temperatures. To reclaim a variety of uses for MgFe$_2$O$_4$ nanopowder, it is worth studying how to control the crystallite size and morphology by a simpler method. We have therefore researched the effect of adding other elements to MgFe$_2$O$_4$ nanopowder. We found that adding Si atoms to MgFe$_2$O$_4$ is useful in preventing its crystallite growth, and notable results were briefly described in a previous report. We have continued to thoroughly investigate the influence of other elements doped on the microstructure, morphology, and specific surface area (SSA) of MgFe$_2$O$_4$, moreover, and have found that La addition is more effective in suppressing crystallite growth than Si addition.

In the present study, we introduce experimental results for La-added MgFe$_2$O$_4$ samples obtained from X-ray diffraction (XRD), Raman scattering spectroscopy, scanning electron microscopy (SEM), N$_2$ adsorption-desorption measurement, and X-ray photoelectron spectroscopy (XPS).

2. Experimental

MgFe$_2$O$_4$ powder was prepared from a malic acid complex. Mg(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and malic acid in a 1:2:3 molar ratio were dissolved in deionized water. La atoms were added to MgFe$_2$O$_4$ using La(NO$_3$)$_3$·6H$_2$O. The amount of La atoms added was set at 5 and 10 mol% with respect to Fe. The solution was heated on a hot plate to prepare the MgFe$_2$O$_4$ precursor powder. The precursor was calcined in the temperature range of 600 to 800°C in air for
2 h. The heating rate was set to 10 °C min⁻¹ in all cases. Powder XRD measurement was carried out to analyze the crystal phase of the prepared sample powders. XRD patterns were corrected with Cu-Kα radiation, sweep rate: 2° min⁻¹ and 30 kV – 20 mA. PDF files were used to identify the crystal phases. The microstructure of the products was observed by SEM (S-5200, Hitachi, Ltd.). Raman spectra were recorded on a Raman spectrometer (in DXR Smart Raman, Thermo Scientific) equipped with a CCD detector at room temperature using a laser diode with 780 nm and laser power 100 mW. The specific surface area and textural properties (pore size, pore volume, and distribution) of materials were evaluated by the gas-adsorption isotherm of N₂ at −196°C following the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The valence state was analyzed by XPS under 10⁻⁶ Pa. XPS spectra were recorded by a JEOL JPS-9010MX spectrometer with Al Kα radiation without pretreatment.

3. Results and discussion

Figure 1 compares the XRD patterns of La-added and pure MgFe₂O₄ powders. These powders were heated at 600 or 800°C in air for 2 h. After calcination at 600°C, no traces of impurities were observed in the La-added or pure MgFe₂O₄ powders. The lattice parameter of pure MgFe₂O₄ was estimated to be \( a = 0.83766 \) nm, which was in good agreement with the reference value (PDF 01-074-8054). Of special note in Fig. 1, the diffraction peak strength for La-added MgFe₂O₄ decreased remarkably in comparison with the pure powder. Similar behavior was observed for Sm-doped MgFe₂O₄, as reported by Thankachan et al. As discussed below, this occurred because La³⁺ has relatively large ionic radii in comparison with Fe³⁺, and the difficulty in crystallization is increased by adding La³⁺ to MgFe₂O₄. After calcination at 800°C, impurity peaks identified as the LaFeO₃ phase (PDF: 01-074-2203) appeared in the XRD pattern of 10 mol % La-added MgFe₂O₄.

Figure 2(a) shows the relationship between the lattice volume and the amount of La-addition. For 600°C-calcined MgFe₂O₄, the lattice volume increased slightly up to 5 mol % and remained almost unchanged at above 5 mol % La addition. For 800°C-calcined MgFe₂O₄, on the other hand, the lattice volume increased up to 5 mol % and then decreased at above 5 mol %. It is well-known that MgFe₂O₄ crystal has an intermediate cation distribution between the normal spinel and inverse spinel structures. Thus, Mg²⁺ and Fe³⁺ occupy both the tetragonal and octahedral sites. The six-fold-coordinated ionic radii of Mg²⁺, Fe³⁺, and La³⁺ were reported as 0.72, 0.55, and 1.03 nm, respectively. The four-fold-coordinated ionic radii of Mg²⁺ and Fe³⁺ were reported as 0.57 and 0.49 nm, respectively, but there are no data for four-fold-coordinated La³⁺. A lattice volume increase with increases in the amount of La³⁺ addition seems to be proper from only the viewpoint of ionic radii. The difference in ionic radii between Fe³⁺ or Mg²⁺ and La³⁺ ions is too large, however, suggesting that the solubility limit of
La into MgFe$_2$O$_4$ was small and that the added La atoms are mainly segregated at the periphery or surface of the MgFe$_2$O$_4$ grains. It should be noted, moreover, that a significant impurity phase such as LaFeO$_3$ was recognized for the MgFe$_2$O$_4$ calcined at 800°C.

To obtain information on the crystallite size and heterogeneous strain for both La-added and pure MgFe$_2$O$_4$ samples, the Williamson-Hall method was applied to the results of the XRD measurements.$^{11}$ Figure 2(b) and Table 1 depict the relationships between the heterogeneous strain in the samples and the calcination temperature and between the crystallite size and the calcination temperature, respectively. The heterogeneous strain of La-added MgFe$_2$O$_4$ decreased with increases in the calcination temperature. As described above, the lattice volume of 10 mol% La-added MgFe$_2$O$_4$ decreases significantly after calcination at 800°C, as shown in Fig. 2(a), and LaFeO$_3$ appeared clearly, as shown in Fig. 1. These results indicate that a small amount of the added La was doped into MgFe$_2$O$_4$ while a large amount of La was segregated at the perimeter or surface of the MgFe$_2$O$_4$ grains.

Figure 3 depicts the Raman spectra obtained for La-added and pure MgFe$_2$O$_4$ after calcination at 600 or 800°C in air for 2 h. After calcination at 600°C, the pure powder showed five spectra at approximately 216, 334, 482, 561, and 712 cm$^{-1}$. These spectra can be ascribed to MgFe$_2$O$_4$, as reported by Wang et al.$^{12}$ One broad Raman mode was also observed at 648 cm$^{-1}$. According to the factor group analysis, the Raman shifts at 216 and 482 cm$^{-1}$ can be assigned to the F$_{2g}$ mode, the two peaks centered at 334 and 561 cm$^{-1}$ to the E$_g$ mode, and the mode centered at 712 cm$^{-1}$ to the A$_{1g}$ mode. When La atoms were added into MgFe$_2$O$_4$, the A$_{1g}$, E$_g$, and F$_{2g}$ modes were significantly weakened. It is known that Raman spectra broaden when lattice defects are introduced into the crystal because of the selection-rule failure for the wave vector.$^{13}$ As expected, in Fig. 1, the crystallinity of the prepared MgFe$_2$O$_4$ is lowered remarkably by La addition, and that the spectrum strength of the A$_{1g}$, E$_g$, and F$_{2g}$ modes decreased.

SEM observation was conducted to investigate the effect of adding La atoms on the morphology and microstructure of MgFe$_2$O$_4$ powder. Figure 4 presents SEM photographs for La-added and pure MgFe$_2$O$_4$ powders. The size of an identifiable primary particle of pure MgFe$_2$O$_4$ is estimated to be approximately 20 nm. In 5 and 10 mol% La-added MgFe$_2$O$_4$ powders, smaller primary particles are observed in comparison with those in pure MgFe$_2$O$_4$ powder. These primary particle sizes for La-added and pure MgFe$_2$O$_4$ powders accord well with the crystallite sizes estimated from the XRD measurement, as shown in Fig. 1.

In order to obtain more detailed information on the microstructures of La-added and pure MgFe$_2$O$_4$ powders, we estimated the pore shapes, total pore volumes, and pore size distributions of the powders from the nitrogen adsorption–desorption isotherms. The results for the nitrogen adsorption isotherms of La-added MgFe$_2$O$_4$ are shown in Fig. 5(a). The total pore volumes of La-added and pure MgFe$_2$O$_4$ powders increased in the relative pressure (P/P$_0$) range of 0.5 to 0.98. La-added and pure powders were classified as type IV, according to the Brunauer-Deming-Deming-Teller (BDDT) scheme.$^{14}$ This result

| Table 1. Crystallite sizes estimated by the Williamson-Hall method |
|-------------------|------------------|------------------|
|                  | 400°C            | 600°C            | 800°C            |
| 0%                | 7.4 nm           | 20.5 nm          | 76.6 nm          |
| 5 mol% La         | 4.7 nm           | 4.5 nm           | 9.1 nm           |
| 10 mol% La        | 2.4 nm           | 2.8 nm           | 7.8 nm           |

![Fig. 3. Raman spectra obtained for La-added and pure MgFe$_2$O$_4$ after calcination at 600 and 800°C in air for 2 h: (a) pure, (b) 5 mol% La-added MgFe$_2$O$_4$, and (c) 10 mol% La-added MgFe$_2$O$_4$ at 600°C; and (d) pure, (e) 5 mol% La-added MgFe$_2$O$_4$, and (f) 10 mol% La-added MgFe$_2$O$_4$ at 800°C.](image-url)
suggests that La-added and pure MgFe₂O₄ powders have a mesoporous structure. In order to analyze the capillary shapes of the samples, moreover, we also measured the nitrogen adsorption–desorption isotherms. Hysteresis loops associated with capillary condensation were observed for all the samples examined, as shown in Fig. 5(b). IUPAC classification of adsorption–desorption hysteresis⁰¹ revealed that MgFe₂O₄ powder contained agglomerated spherical particles (type H1, formerly type A), whereas La-added MgFe₂O₄ powders had disordered pores (type H2, formerly type E), which are often referred to as ‘cylindrical’ and ‘ink bottle’ pores, respectively. The addition of La to MgFe₂O₄ caused suppression of crystal growth, and the capillary shapes varied from cylindrical to ink bottle, causing a change in pore volume.

The BJH pore size distribution was calculated from a branch of the nitrogen desorption isotherms. Figure 6 shows the BJH pore size distribution of La-added and pure MgFe₂O₄ powders after heating at 600°C in air for 2 h.
MgFe₂O₄ powders. For pure MgFe₂O₄ powder, a large peak was observed in the range of 4 to 12 nm, and the representative pore size was a maximum of around 10 nm. For La-added MgFe₂O₄ powder, on the other hand, a large peak was observed in the range of 3 to 4 nm. The SSA of pure MgFe₂O₄ powder calcined at 600°C was 35.2 m² g⁻¹, as determined by applying the least squares method to the BET plot. When 5 and 10 mol % La was added to MgFe₂O₄, the BET surface area increased slightly to 81.0 and 84.9 m² g⁻¹, respectively.

The chemical valence states of La-added and pure MgFe₂O₄ powders were also examined by XPS measurements. Figure 7 shows XPS spectra of Mg 2s, Fe 2p, O 1s, and La 3d for pure and La-added MgFe₂O₄ powder in comparison with those for the pure powder. A charge correction was performed by centering the C 1s spectrum at 285.0 eV. The O 1s signal appeared at around 531.0 eV with an accompanying shoulder. The main peak comes from lattice oxygen, and the shoulder corresponds to oxygen adsorbed at the surface of MgFe₂O₄. The binding energies of the Mg 2s, Fe 2p, and La 3d signals are in good agreement with the Mg²⁺, Fe³⁺, O²⁻, and La³⁺ valence states.

4. Conclusion

In conclusion, there were no traces of an impurity phase in 5 mol % La-added MgFe₂O₄ in the XRD measurement, while the LaFeO₃ phase was clearly observed in 10 mol % La-added powder. The crystallite growth was remarkably suppressed by La doping. The primary particle sizes seem in SEM photographs were consistent with the crystallite size estimated from the XRD measurements. From the nitrogen adsorption–desorption isotherm measurement, it was found that the addition of La to MgFe₂O₄ caused suppression of crystal growth and that the capillary shapes varied from cylindrical to ink bottle, leading to changes in the pore volume and pore size distribution. The binding energies of the Mg 2p, Fe 2p, O1s, and La 3d signals were also in good agreement with the Mg²⁺, Fe³⁺, O²⁻, and La³⁺ valence states in the XPS measurement.

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