Suppression of Jahn–Teller distortion by chemical pressure of SiO₂ and local structure analysis of CuFe₂O₄ nanoparticles

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CuFe₂O₄ nanoparticles encapsulated by different amounts of amorphous SiO₂ were prepared by a wet chemical method. These nanoparticles were characterized by X-ray diffraction and X-ray absorption fine structure analysis and found to have either a tetragonal or a cubic structure depending on the amount of SiO₂. Magnetization measurements were performed for all samples using a SQUID magnetometer. The tetragonal nanoparticles showed a smaller maximum magnetization (Mₛ) and a larger coercive force (Hᵥ) than the cubic nanoparticles.

Keywords: Extended X-ray absorption fine structure (EXAFS), Magnetic measurements, Iron oxide, Nano-particles, Magnetization, Nanostructures

1. Introduction

Magnetic nanoparticles have long been of scientific and technological interest. Spinel-structured ferrite nanoparticles with the formula MFe₂O₄ where M represents a divalent metal ion are the most famous magnetic materials and have been used in many industrial applications. The magnetic properties of ferrite nanoparticles were drastically changed by varying the M⁺⁺⁺ ions and their particle size, which suggests that there are many possibilities for their application by the optimization of their magnetic properties. In recent years, ferrite nanoparticles have also been investigated for biomedical applications such as magnetic resonance imaging (MRI) enhancement, drug delivery, and heating agents for magnetic hyperthermia.

Copper ferrite (CuFe₂O₄) occurs in two structures: tetragonal and cubic. In general, the tetragonal structure is more stable at room temperature and transforms to the cubic structure when heated above about 633–713 K. In CuFe₂O₄ bulk materials, most of the Cu⁺⁺ ions occupy the octahedral B sites, meaning that the cation distribution is inverse. Due to this distribution, the orbital overlap between Cu²⁺ and O²⁻ is induced and the octahedral B site distorts from the cubic structure to tetragonal symmetry, which is known as the Jahn–Teller effect. Jahn–Teller distortion only occurs at the B-site; therefore, the distribution of Cu ions affects the structure. The magnetization of CuFe₂O₄ is affected by this distortion; the cubic structure has a higher magnetization than the tetragonal structure.

Although CuFe₂O₄ nanoparticles can be synthesized by combustion, sol-gel, co-precipitation, mechanical milling, and solid-state reactions, there are only a few methods for obtaining size-controlled cubic Cu-ferrite because its structure is greatly affected by the production conditions. For example, the lattice structure is affected by various factors such as lattice defects and heating and cooling speeds. These phenomena are probably caused by the small energy difference between the Cu⁺⁺⁻ ions that are present at the A-site and B-site. In our previous studies, we have shown that Cu-ferrite nanoparticles could be obtained by a wet chemical method and that particle diameter can be controlled. Furthermore, it was possible to encapsulate nanoparticles with amorphous SiO₂ and the structure of Cu-ferrite was affected by the state of the SiO₂. In the present work, we conducted a detailed study of the CuFe₂O₄ nanoparticles encapsulated by varying amounts of SiO₂. The CuFe₂O₄ nanoparticles were synthesized by the wet chemical method and their fine structure was studied by X-ray diffraction (XRD), X-ray fluorescence (XRF) and X-ray absorption fine structure (XAFS). The magnetic properties of the nanoparticles were also evaluated.

2. Experimental

CuFe₂O₄ nanoparticles surrounded by different amounts of amorphous SiO₂ were synthesized by a wet chemical method. Aqueous solutions of CuCl₂·2H₂O, FeCl₃·6H₂O, Na₂SiO₃·9H₂O, and NaOH were mixed to obtain a precipitate by neutralization. The mole ratio of the prepared reagent was Cu:Fe:Si = 1:2:n (n = 0, 0.5, 2, 3, 4) and the amount of SiO₂ was varied according to the mole ratio of Na₂SiO₃·9H₂O and NaOH concentration. The obtained precipitates were washed three times with distilled water and dried at about 350 K. The as-prepared samples were then subjected to heat treatment in a furnace under air and at annealing temperatures of ~1023 K, forming CuFe₂O₄ in nSiO₂ (n = 0, 0.5, 2, 3, 4) nanoparticles.

All of the prepared samples were examined by XRD (Cu-Kα, λ = 0.154 nm). The average particle sizes of these samples were estimated by the Scherrer formula and crystallite size distribution analysis software CSDA (RIGAKU). The lattice constants were also calculated by Rietveld analysis using Rietveld FP software. In addition, we performed XRF analysis to examine their composition ratios.

X-ray absorption fine structure (XAFS) measurements were performed to clarify the structures of the nanoparticles. The Cu–K edge (8980.3 eV) and Fe–K edge (7,111.2 eV) XAFS spectra were measured in the range of the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectra were obtained using the transmission method with a Si(111) monochromator at the BL-9C and BL-12C station in the Photon Factory synchrotron radiation facility, KEK, Japan. The cation distribution and atomic distances of samples were analyzed using the fitting software REX2000.

Magnetization measurements were performed using a SQUID magnetometer (Quantum Design, MPMS). Magnetization curves were measured at 5 K in the ±50 kOe applied magnetic field.

3. Results and Discussion

3.1 XRD analysis

Figure 1 shows the XRD patterns of CuFe₂O₄ in nSiO₂ (n = 0, 0.5, 2, 3, 4) nanoparticles annealed at 1023 K. All samples showed a broad peak around 2θ = 23° that corresponded to...
amorphous SiO$_2$. It was evident that these patterns were affected by the amount of SiO$_2$. The average particle diameters were estimated from the broadening of the diffraction peaks using Scherrer's formula and CSDA and the estimated diameters of all samples were controlled at around 12 nm. The particle diameters were also confirmed by the TEM image (Figure 2). The samples that were rich in SiO$_2$ ($n = 2, 3, 4$) showed a single cubic spinel phase (Fd$ar{3}$m). However, the samples without silica ($n = 0$) and insufficient SiO$_2$ ($n = 0.5$) showed multiphase patterns that indicated both cubic and tetragonal spinel phases. Table 1 shows the lattice constants calculated by Rietveld analysis. The axis ratio of the $n = 0$ sample that showed tetragonal phase was $c/a = 1.48$.

By the SiO$_2$ encapsulation, the lattice constants $a$ and $b$ were increased and the lattice structure became cubic. It was considered that the distortion that was caused by different lengths between Cu-O was suppressed by SiO$_2$ coating. For the cubic samples $n = 2, 3, 4$, the lattice constants showed almost the same value, so the cubic lattice structure was unchanged by the SiO$_2$ amount. XRF measurements confirmed that the composition ratio of Cu:Fe maintained the preparation ratio. For the SiO$_2$, while the ratios were decreased from the preparation ratio, the ratio was changed by $n$. These XRD patterns led to the conclusion that the crystal structures were affected by the amount of SiO$_2$ and the CuFe$_2$O$_4$ nanoparticle's structure became cubic after encapsulation with sufficient SiO$_2$, $n \geq 2$.

Owing to encapsulation by amorphous SiO$_2$, CuFe$_2$O$_4$ was produced with a cubic spinel phase. It is plausible that the amorphous SiO$_2$ layer suppresses the Jahn–Teller distortion because of pressure from the encapsulated SiO$_2$. When decreasing the amount of amorphous SiO$_2$ by using a smaller mole ratio $n$, the pressure was weakened, which promoted distortion and formed the tetragonal phase.

### 3.2 XAFS analysis

To investigate the Jahn–Teller distortion and the effect of encapsulation by amorphous SiO$_2$ on Cu-ferrite nanoparticles, we performed XAFS measurements and analyzed their fine structures. Using XAFS analysis, structural changes such as cation distributions and atomic distances were observed$^{[50]}$.

Figure 3 shows the results of the Fourier transformation of the $k^2$-weighted Cu–K edge and Fe–K edge EXAFS spectra. In Figure 3(a–d), the first peak at ~1.5 Å corresponds to the distance between the metal ion and its nearest neighbor oxygen atom (M–O). The second peak at ~2.6 Å represents the distance between the two cations in the octahedral B sites (B–B). The third peak at ~3.1 Å represents the distance between a cation in an octahedral B site and a cation in a tetrahedral A site (B–A).

![Figure 3](image-url)

Table 1. The particle diameter and lattice constant values as calculated using the XRD patterns.

<table>
<thead>
<tr>
<th>SiO$_2$ amount, $n$</th>
<th>$a$ / Å</th>
<th>$b$ / Å</th>
<th>$c$ / Å</th>
<th>$c/a$</th>
<th>Lattice structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>8.36</td>
<td>8.36</td>
<td>8.36</td>
<td>1</td>
<td>Cubic</td>
</tr>
<tr>
<td>3</td>
<td>8.35</td>
<td>8.35</td>
<td>8.35</td>
<td>1</td>
<td>Cubic</td>
</tr>
<tr>
<td>2</td>
<td>8.35</td>
<td>8.35</td>
<td>8.35</td>
<td>1</td>
<td>Cubic</td>
</tr>
<tr>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Cubic and Tetragonal</td>
</tr>
<tr>
<td>0</td>
<td>5.84</td>
<td>5.84</td>
<td>8.64</td>
<td>1.48</td>
<td>Tetragonal</td>
</tr>
</tbody>
</table>

Table 2. The composition ratios of CuFe$_2$O$_4$ in $n$SiO$_2$ ($n = 0, 0.5, 2, 3, 4$) nanoparticles measured by XRF. The ratios were normalized to become Cu$_{n}$Fe$_2$O$_4$ in $n$SiO$_2$.

<table>
<thead>
<tr>
<th>SiO$_2$ amount $n$</th>
<th>Cu amount $\alpha$</th>
<th>Fe amount $\beta$</th>
<th>Si amount $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.03</td>
<td>1.97</td>
<td>1.65</td>
</tr>
<tr>
<td>3</td>
<td>1.07</td>
<td>1.93</td>
<td>1.54</td>
</tr>
<tr>
<td>2</td>
<td>0.96</td>
<td>2.04</td>
<td>0.98</td>
</tr>
<tr>
<td>0.5</td>
<td>1.00</td>
<td>2.00</td>
<td>0.31</td>
</tr>
<tr>
<td>0</td>
<td>0.98</td>
<td>2.02</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 2. TEM image of 12-nm CuFe$_2$O$_4$ in 4SiO$_2$ nanoparticles.
peaks were single for all samples and the peak intensity weakened as the amount of SiO₂ decreased. The EXAFS spectra consisted of the superposition of sine waves with wavelengths that correspond to the respective atomic distance where similar wavelengths cancel each other out. The weak intensity Cu–O peaks may be explained by the Jahn–Teller distortion effect in this sample’s CuO₆ octahedron. Figure 3(a) only showed the B–B peak at ~2.6 Å and no peaks corresponded to the B–A bond at 3.1 Å in the n = 0 and 0.5 samples. However, for the n = 4 sample, there were small shoulders at 3.1 Å that corresponded to the B–A bond. This result suggested that Cu²⁺ ions only became distributed in the tetrahedral A site when n = 4, and this was a typical feature of the cubic structure of Cu-ferrite nanoparticles.

Figures 3(c) and (d) show the Fe–K edge spectra of the CuFe₂O₄ in nSiO₂ (n = 0, 0.5, 4) samples. The B–B and B–A peaks indicate that the Fe ions occupy both the tetrahedral A sites and the octahedral B sites. Each sample exhibited nearly equal intensities for the B–B and B–A peaks with the n = 0 and 0.5 samples. Therefore, the ratio of Fe ions in the tetrahedral A sites and octahedral B sites would be 1:1. However, the n = 4 sample showed a higher B–B peak than B–A peak, which indicated that the quantity of iron ions distributed in B-site was increased. This result showed good agreement with the result of the Cu–K edge EXAFS spectra. Increasing the amount of Cu²⁺ ions in the A-site squeezed Fe ions into the B-site. This indicated that the ion distribution was closely related to the lattice structure. The distribution change in the metal ions produced the cubic structure of Cu ferrite.

Based on these results, we assumed that the Cu ions occupied

Table 3. M-O length of CuFe₂O₄ in nSiO₂ (n = 0, 0.5, 4) nanoparticles obtained by EXAFS spectra.

<table>
<thead>
<tr>
<th>SiO₂ amount, n</th>
<th>Cu-O length / Å</th>
<th>Fe-O length / Å</th>
<th>Lattice structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.49</td>
<td>1.50</td>
<td>Cubic</td>
</tr>
<tr>
<td>0.5</td>
<td>1.50</td>
<td>1.49</td>
<td>Cubic &amp; Tetragonal</td>
</tr>
<tr>
<td>0</td>
<td>1.50</td>
<td>1.49</td>
<td>Tetragonal</td>
</tr>
</tbody>
</table>
From the composition ratio obtained by XRF analysis. The magnetization value $M$ were expressed by $\mu_0$ unit. The saturation magnetization ($M_s$) of the nanoparticles depends on various amounts of SiO$_2$; with $n = 0, 0.5, 2,$ and $4$, $M_s$ is 1.40, 1.50, 1.78 and 1.94 $\mu_0$, respectively. These results show that the tetragonal spinel samples ($n = 0, 0.5$) have lower saturation magnetization values than the cubic samples ($n = 2, 4$). Here, it was expected that the A–B distance (Fe–Cu distance) of the samples that contain less SiO$_2$ would be shorter than that of the cubic samples because of Jahn–Teller distortion. Thus, different values for the saturation magnetization in Fig. 4 suggest that the interactions between the antiferro-coupling sites A and B change with the A–B distance. This variation in the A–B distance depends on the Cu–O distance caused by Jahn–Teller distortion. The $M_s$ values differed between the cubic samples with $n = 2$ and 4. The distribution ratios were calculated using their magnetization values and composition ratio: the obtained results were (Cu$_{0.078}$Fe$_{0.922}$)$_2$[Cu$_{0.882}$Fe$_{1.118}$]O$_4$ for the $n = 2$ sample and (Cu$_{0.131}$Fe$_{0.867}$)[Cu$_{0.897}$Fe$_{1.103}$]O$_4$ for the $n = 4$ sample. From the above, we could confirm that the samples with sufficient silica ($n \geq 2$) gained a cubic structure and that the Cu$^{2+}$ distribution was changed by their structure. For the cubic samples $n = 2$ and 4, the lattice constant and their composition ratio of metal ions were almost the same. The difference in the samples was only in the amount of SiO$_2$. These results showed that the difference in $M_s$ between the cubic samples with $n = 2$ and 4 was caused by their different distributions of metal ions. This implied that the Cu$^{2+}$ ions distribution was changed by the SiO$_2$ amount for the cubic samples.

### 4. Conclusions

The SiO$_2$ encapsulation effects were investigated for the CuFe$_2$O$_4$ nanoparticles. The Cu ferrite encapsulated by different amounts of amorphous SiO$_2$ was synthesized using a wet chemical method. XRD patterns showed that the structure of the nanoparticles was changed by the amount of added SiO$_2$ and their particle diameters were controlled around 12 nm. EXAFS analysis clarified that the encapsulation by amorphous SiO$_2$ distributed Cu ions into the tetrahedral A-site and the structure became cubic upon sufficient silica encapsulation. Magnetization measurements showed that the cubic-structure sample had a higher $M_s$ value than that of the sample with the tetragonal structure. This result was caused by the change in the lattice structure and the difference in Cu$^{2+}$ ions distribution.

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### References

27) Y. Uehara: Zairyou, 22, pp. 96 (1973)

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