Synthesis and characterization of $CoFe_2O_4$ magnetic nanoparticles prepared by temperature-controlled coprecipitation method

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Abstract

Magnetic nanoparticles of cobalt ferrite ($CoFe_2O_4$) have been synthesized in a homogeneous aqueous solution without any template and subsequent heat treatment. The average particle size could be varied in the range of 2–14 nm by controlling coprecipitation temperature of Co^{2+} and Fe^{3+} ions in alkaline solution although the size distribution is pretty wide. As the precipitation temperature increased in the range of 20–80°C, the average particle size also increased. However, there is a considerable change in XRD crystallinity and the average size of the nanoparticles at the precipitation temperature between 40°C and 60°C. While the nanoparticles prepared at the temperature below 40°C show superparamagnetic relaxation at room temperature with blocking temperatures between 75 and 200 K, the samples prepared at the temperature higher than 60°C consist of both superparamagnetic and ferrimagnetic nanoparticles that result in magnetic coercivity at room temperature. Mössbauer spectra of the samples also confirmed their magnetic properties and wide size distribution in each sample. The analysis of the spectra gave a rough estimation of the ratio of superparamagnetic and ferromagnetic nanoparticles in each sample at various temperatures.
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1. Introduction

Spinel ferrite nanoparticles have been intensively investigated in recent years because of their remarkable electrical and magnetic properties and wide practical applications to information storage system, ferrofluid technology, magnetocaloric refrigeration and medical diagnostics. Among spinel ferrites, cobalt ferrite, $CoFe_2O_4$ is especially interesting because of their high cubic magnetocrystalline anisotropy, high coercivity and moderate saturation magnetization. Recently, cobalt ferrite nanoparticle was also known to be a photomagnetic material which shows

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an interesting light-induced coercivity change [1,2].

A lot of synthetic strategies for preparing nano-sized cobalt ferrite have been presented. Pileni et al. utilized oil-in-water micelle to prepare size-controlled Co-ferrite in the range of 2–5 nm [3]. Zhang et al. [4] also reported the nanoparticles of 2–35 nm in diameter which were prepared in normal micelle similarly with the method of Pileni et al. Shah [5] and Ahn [6] used water-in-oil microemulsion to prepare the nanoparticles in the diameter of 50 and 4.9 nm, respectively after heat treatment. Block copolymer was also used as a template to prepare the cobalt ferrite nanocluster of 15 nm in diameter at room temperature [7]. In homogeneous aqueous solution, the hydrothermal condition was usually employed to obtain the ferrite nanoparticles by coprecipitation of Fe^{3+} and Co^{2+} ions in alkaline aqueous solution [8]. Morais et al. showed the size-controlled synthesis of the nanoparticles of 10–15 nm in aqueous solution at 95°C by controlling stirring speed [9]. Rajendrain et al. demonstrated 6–20 nm sized cobalt ferrites prepared in aqueous solution at room temperature by the oxidative coprecipitation of Fe^{2+} and Co^{2+} [10]. The microemulsion techniques for preparing ferrite nanoparticles must give a better size control than the coprecipitation method in homogenous solution do. However, their application can be limited due to the surfactants that are covered on the surface of the ferrite particles and hard to be removed.

The size and magnetic properties of cobalt ferrite nanoparticles prepared by the coprecipitation method can be greatly varied depending on pH, salt concentration, temperature, stirring speed, counterion nature, etc. As far as we know, there is no systematic study for the effect of the precipitation temperature on the formation of $CoFe_2O_3$ in homogeneous aqueous solution by the coprecipitation method. The aim of this work is to investigate the temperature effect on the size of $CoFe_2O_4$ nanoparticles prepared in alkaline aqueous media without any subsequent calcination and characterize their magnetic properties with the measurements of field and temperature-dependent magnetization and Mössbauer spectroscopy.

2. Experimental

2.1. Synthesis of CoFe₂O₄ nanoparticle

The solution mixture of 14.35 ml of 0.697 M $FeCl_3 \cdot 6H_2O$ (98% +, Aldrich) and 7.90 ml of 0.632 M $CoCl_2 \cdot 6H_2O$ (extra pure, Junsei) both in 0.4 M HCl was drop-by-drop added to 200 ml of 1.5 M NaOH solution which was previously adjusted to pH 12 with concentrated HCl. The precipitation occurred immediately to change the reaction solution to dark brown. During the precipitation, the reaction solution was vigorously stirred with a constant speed and kept pH 11–12 by adding 1.5 M NaOH solution. The precipitation temperature was maintained constant within ±1°C with a water-jacketed reaction vessel using circulating thermostatic bath. The precipitates were kept stirred in the reaction solution for 2 h at the desired constant temperature and separated by being centrifuged at 10000 rpm for 20 min. The resulting precipitates were washed with deionized water and the centrifugation and washing were repeated about 10 times until a chloride ion is free from the washed water. The washed samples were dried at room temperature under vacuum for 24 h. The water used here was purified with distillation and Barnstead Nanopure System II. For the reaction solution the water was boiled to remove resolved carbon dioxide before use. All other chemicals were reagent grade and used as received.

2.2. Apparatus

X-ray diffraction (XRD) patterns were measured by Phillips X'pert MPD system with CuK_α source and $0.0046°/s$ scan rate. Transmission electron micrographs (TEM) and electron diffraction patterns were taken with Jeol JEM 2010 operated at 200 kV. Magnetization measurements were carried out with Quantum Design MPMS 7 SQUID magnetometer. Temperature dependence of magnetization was measured under the field of 100 G. Mössbauer spectra were measured by Fast Comtech FG-351 system with ^{57}Co source doped in metallic rhodium that was oscillated in a sinusoidal mode.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of the samples prepared at various temperatures. While the samples, prepared at the temperatures of 20°C (denoted as A) and 40°C (denoted as B), showed broad and unresolved peaks, the samples, prepared at the temperatures of 60°C (denoted as C) and 80°C (denoted as D), showed the clear pattern which corresponds to well known structure of $CoFe_2O_4$ which has a cubic, spinel type lattice [11]. For the samples of C and D, the unit cell parameter a is estimated as 8.373($\pm$0.003) and 8.397($\pm$0.001) Å, respectively using Nelson–Riley extrapolation [12]. These values are close to the known of bulk $CoFe_2O_4$ (8.395$\pm$0.005) [13]. From the peak of the reflection (3 1 1), we have estimated the particle sizes of the samples using Debye–Scherrer equation [12]. For this calculation the four peaks of (2 2 0), (3 1 1), (2 2 2) and (4 0 0) were deconvoluted to Lorentzian curves using nonlinear curve fitting and the average diameters were estimated with the full-width at half-maximum of the (3 1 1) peak (see Fig. 2). The results are summarized as D_{XRD} in Table 1. As the synthetic temperature increased, the average particle size increased. However, this increment is not smooth. As it can be seen in Fig. 1, the XRD pattern of the

sample C prepared at 60°C is clearly differentiated from that of the sample B prepared at 40°C, while the samples prepared at 20°C and 40°C are very similar. There is somehow a transition in the aspect of size and XRD crystallinity between the samples B and C which were prepared at 40°C and 60°C, respectively.

In Fig. 3, the images of transmission electron microscope for the samples A and C prepared at 40°C and 60°C are shown comparatively. Even though the images are not well resolved due to the diffuse nature and the aggregation of the particles, there can be seen explicitly the size difference between two samples. While the particles of sample A is relatively uniform with about 2–3 nm size, the sample C shows large size distribution in the range of about 4–15 nm. The image of the sample B (not shown here) is not distinctive with that of the sample A. The rough estimations of the average diameters for the four samples are also listed in Table 1. The results are consistent with that from XRD data. Fig. 4 shows the selected-area electron diffraction ring patterns of the nanoparticles prepared at 20°C and 60°C. The pattern for the sample C is well resolved at (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) reflections as in XRD patterns. Although the pattern for the sample B is not well resolved as much as that of
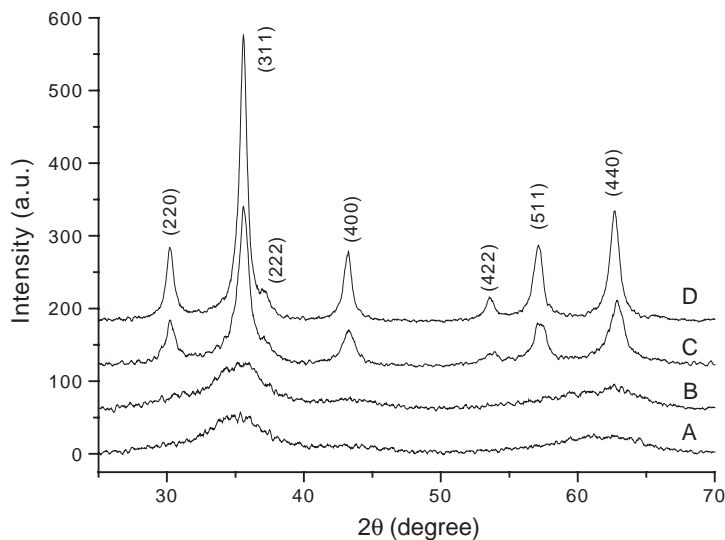

Fig. 1. XRD patterns of $CoFe_2O_4$ nanoparticles prepared at various temperatures: 20°C(A), 40°C(B), 60°C(C), 80°C(D).
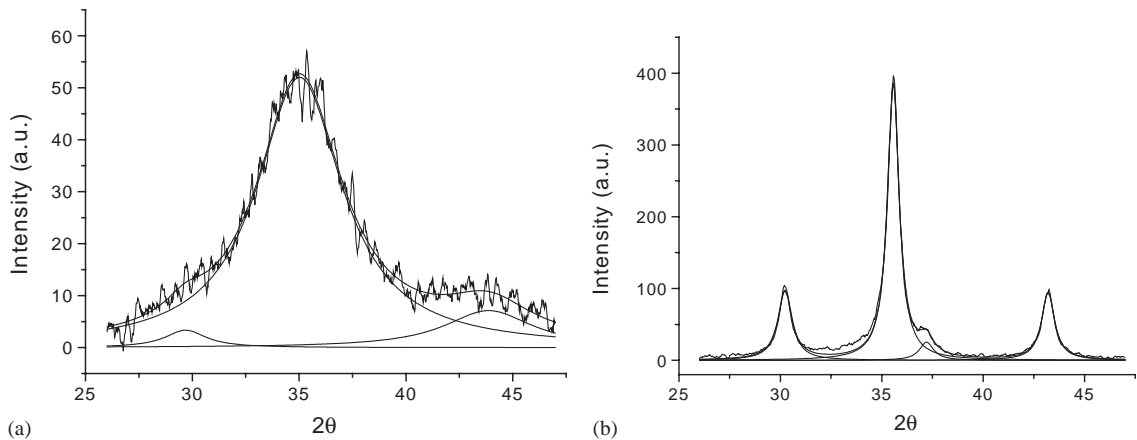
Fig. 2. The fitted XRD peaks of reflection (2 2 0), (3 1 1), (2 2 2) and (4 0 0) for $CoFe_2O_4$ nanoparticles prepared at $20°C$(a) and $80°C$(b). The (2 2 2) reflection in (a) was neglected due to too small contribution.

Table 1
Summaries of some properties of $CoFe_2O_4$ nanoparticles derived from XRD, TEM, magnetic measurements and Mössbauer spectra

Samples	Precipitation temperature (°C)	Lattice parameter (Å)	D_{XRD} (nm)	D_{TEM} (nm)	Magnetization at 10 kOe (emu/g)	H_c (Oe) at 300 K	T_B (K)[a]	T_B (K)[b]
A	20	8.171	2.0	2	2.0	0	75	∼80
B	40	8.358	2.3	3	4.2	0	210 (80)	∼80
C	60	8.373	9.2	8	36	39	>300	420
D	80	8.397	13.8	15	58.3	193	>300	>550

[a] Estimated from the temperature-dependent magnetization curve.
[b] Estimated from Mössbauer spectra measured at various temperatures.

sample C, the reflections of (3 1 1), (4 0 0) and (4 4 0) planes are clearly seen. From the assigned d values, the lattice parameter a was also estimated as 8.171 and 8.358 Å for the samples prepared at $20°C$ and $40°C$, respectively. These values are smaller than those of the samples prepared at $60°C$ and $80°C$, which is close to that of bulk cobalt ferrite. This indicates that there are more defect sites in these nanoparticles than in the samples C and D.

The room temperature magnetizations for applied magnetic field are shown in Fig. 5. The magnetizations for the samples A and B are very weak and are not saturated at the field of 10 kOe. They did not show any coercivity at this temperature. This is characteristic of superparamagnetism. The magnetizations of the samples C and D are much higher and tend to be saturated at a high field. The magnetization values at 10 kOe are 36.0

and 58.3 emu/g for the samples C and D, respectively. The value for sample D is close to the saturation magnetization of bulk cobalt ferrite, known as 65 emu/g [13]. And the magnetization curves show hysteresis with the coercivities (H_c) of 39 and 193 Oe at 300 K for the samples C and D, respectively. These values are much smaller than that of the bulk ferrite, 980 Oe [13]. Although the critical size of cobalt ferrite showing superparamagnetic relaxation at room temperature is not theoretically known, it has been known that $CoFe_2O_4$ in the size range of 10–30 nm shows no superparamagnetic relaxation up to room temperature [14,15]. It can be inferred that the critical size of $CoFe_2O_4$ for superparamagnetic relaxation at room temperature lies roughly between 4 and 9 nm from our results. Fig. 6 shows the temperature dependences of magnetization for those samples measured at the zero-field-cooled
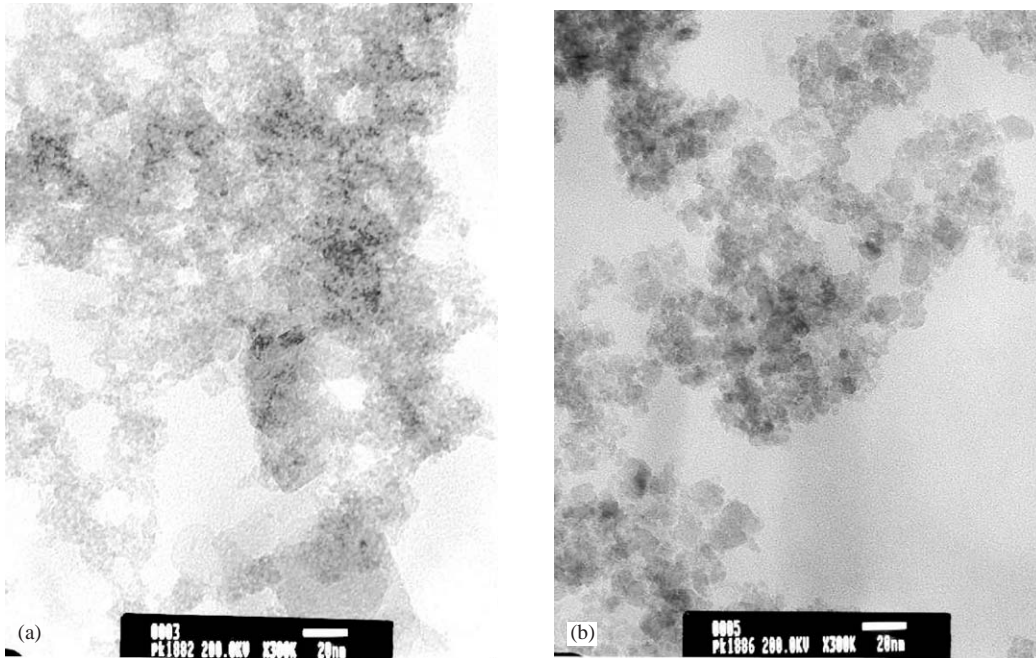
Fig. 3. TEM micrographs of $CoFe_2O_4$ nanoparticles prepared at $40°C$(a) and $60°C$(b).
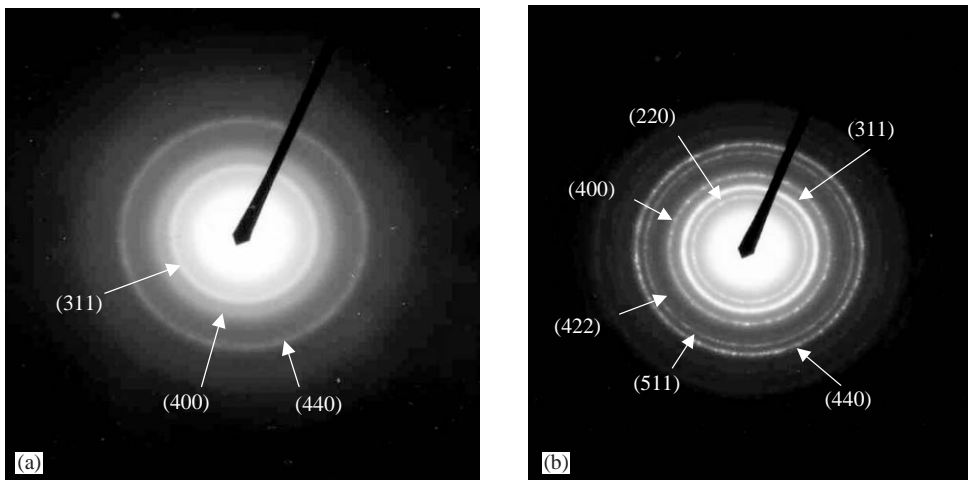

Fig. 4. Selected area electron diffraction patterns of the sample B(a) and sample C(b).

condition. While there are maximum magnetiza-tions below room temperature for the samples A and B, the magnetizations for the samples C and D are continuously increased up to room tempera-ture. This means that while the samples A and B have the blocking temperatures, at which the superparamagnetic relaxation starts to appear, below room temperature, the samples C and D have them above room temperature. The ave-rage blocking temperatures (T_B) for the sam-ples A and B can be estimated as 75 and 210 K, respectively, from the temperatures of the
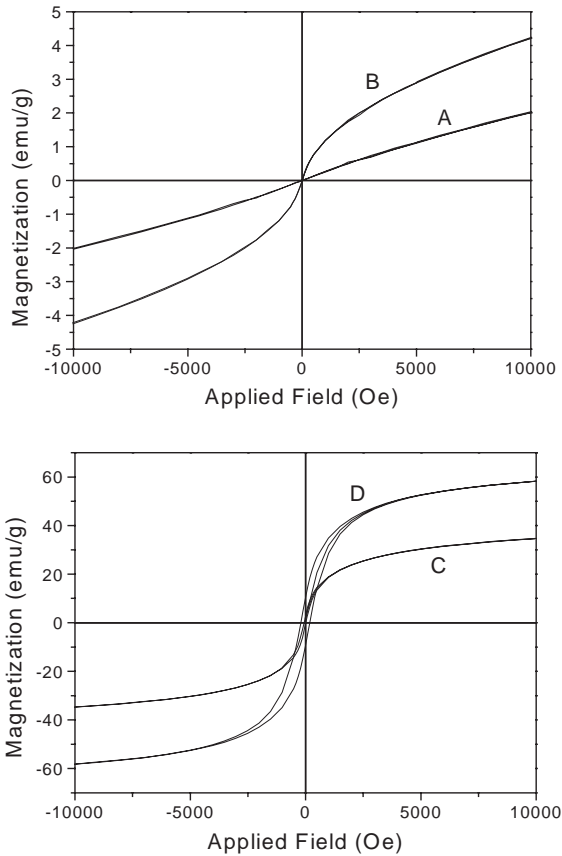
Fig. 5. Magnetization curves versus magnetic field for $CoFe_2O_4$ nanoparticles prepared at various temperatures: 20°C (A), 40°C (B), 60°C (C) and 80°C (D).

Fig. 6. Temperature dependence of zero-field cooled magnetization of $CoFe_2O_4$ nanoparticles prepared at various temperatures: 20°C (A), 40°C (B), 60°C (C) and 80°C (D).

maximum magnetizations. For the sample B, it seems to be consisted of apparently two components that gives two different blocking temperatures since there is a shoulder at around 80 K in the temperature-dependent magnetization curve. It is interesting that the magnetic properties of the samples A and B are considerably different, despite their sizes and crystallinities are not much different as shown in XRD and TEM. This difference might be explained by the difference of size distribution in two samples. If the sample B has a wider size distribution than the sample A has, even though the average particle size is not much different from that of the sample A, the total magnetization will be dominated by the larger particles because the magnetization of
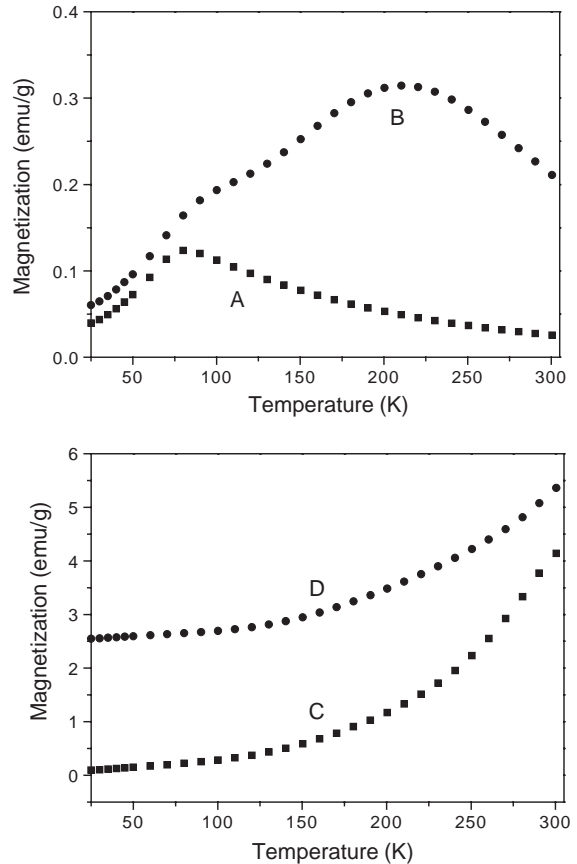
the larger particles is much greater than the smaller particles.

We have measured ^{57}Fe Mössbauer spectra of all samples prepared here at various temperatures in order to study the superparamagnetic nature and the size distribution. Fig. 7 shows the spectra measured at room temperature. As shown in magnetization measurement there is clear difference between the spectra of the samples prepared at 20°C and 40°C and those prepared at 60°C and 80°C. While the formers show a quadrupole doublet which is due to superparamagnetic relaxation, the latters have a complex hyperfine structure in which a quadrupole doublet is superimposed on a magnetically split sextet as shown in the fitted curve. This indicates that the samples C and D can
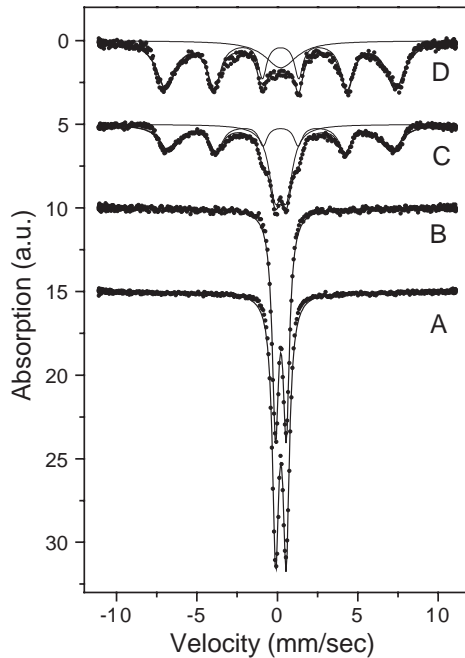
Fig. 7. Mössbauer spectra of CoFe$_2$O$_4$ nanoparticles measured at room temperature. The spectra are denoted as indicated in text.
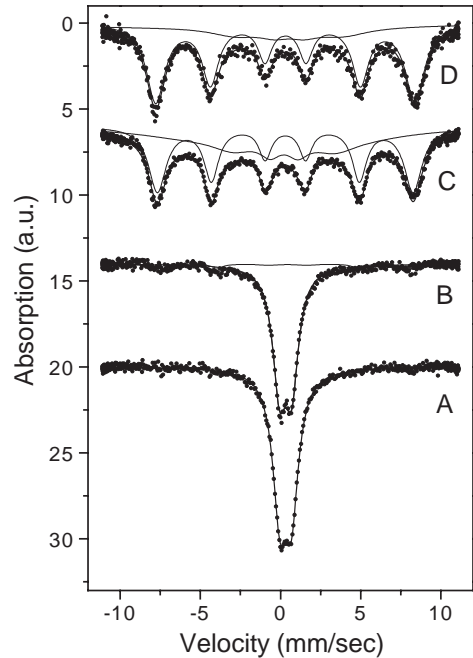

Fig. 8. Mössbauer spectra of CoFe$_2$O$_4$ nanoparticles measured at 125 K.

be divided into two components of superparamagnetic and ferrimagnetic due to wide size distribution. When the measurement temperature decreases to 125 K, the doublets are disappeared in the samples C and D and the sextet starts to appear in sample B as shown in Fig. 8. When the temperature decreases further to 81 K, the sextets in the samples C and D become more pronounced and the superparamagnetic component in samples A and B is markedly decreased as shown in Fig. 9. For the samples C and D, the spectra were measured at the temperatures higher than room temperature in order to find the temperature where the superparamagnetic relaxation is dominant. In Fig. 10 the sample D shows the pronounced superparamagnetic relaxation at 550 K. As shown in all Mössbauer spectra measured here, each spectrum was fitted to one quadrupole doublet or the sum of a doublet and a magnetically split sextet except the spectra of the samples C and D at 81 K which was fitted to the sum of two or three sextets. From the ratio of the doublet area to the sextet area, we have estimated the fraction of
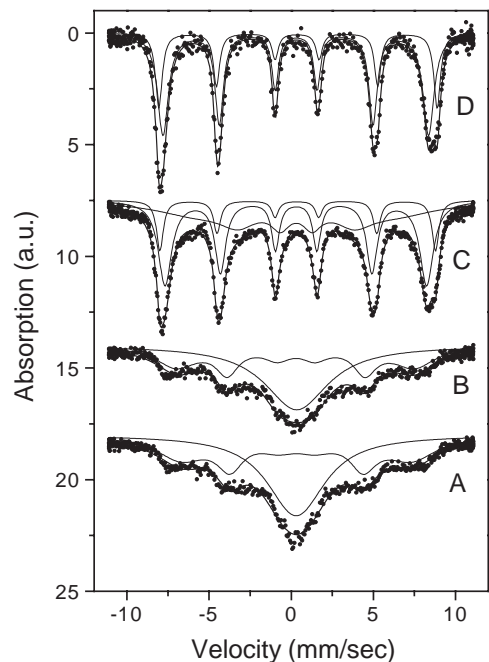

Fig. 9. Mössbauer spectra of CoFe$_2$O$_4$ nanoparticles measured at 81 K.

superparamagnetic components in those samples at various temperatures. The results are shown in Fig. 11. While the change of the superparamag-
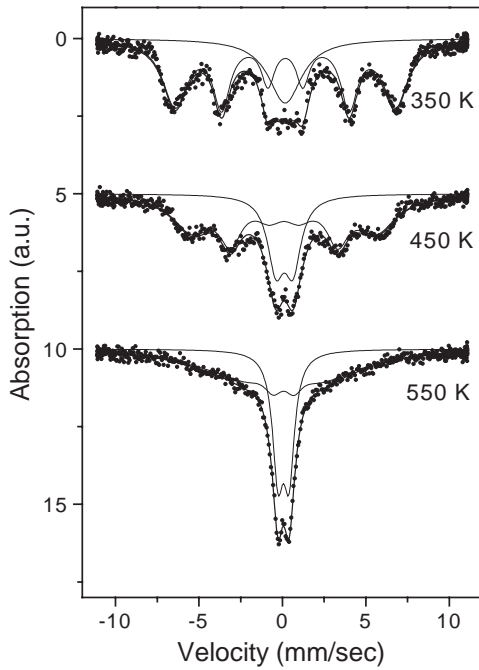
netic fraction for the samples A and B occurs at narrow temperature range, the change for the samples C and D occurs at wider temperature range. This implies that the size distribution in the samples A and B is narrower than in the samples C and D. This was confirmed from the TEM images of Fig. 3.

The blocking temperature can be also defined as a temperature at which the magnetically split and unsplit components represent 50% each of the Mössbauer spectral area. From Fig. 11, the blocking temperatures can be estimated as about 80 K for the samples A and B, 420 K for the sample C and higher temperature than 550 K for the sample D. For the sample B, this value is smaller than the value estimated from the tem-perature-dependent magnetization (210 K). As mentioned above, the magnetization curve for the sample B showed that the sample consisted of two different average sizes of particles: one has T_B at 210 K and the other has T_B at 80 K. Although the magnetization maximum appeared at 210 K, the major particles might be the particles with T_B of 80 K since the magnetization is much higher for larger particles.

The blocking temperature estimated from Mössbauer spectra cannot be consistent with that from the temperature dependence of
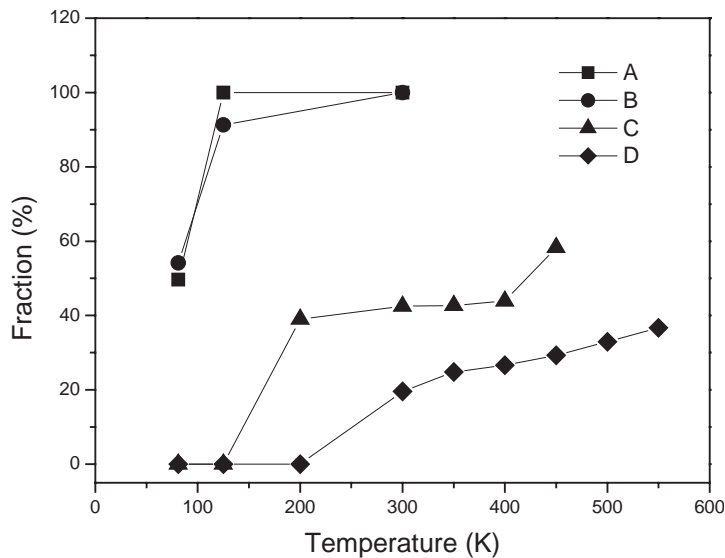

Fig. 10. Mössbauer spectra of $CoFe_2O_4$ nanoparticle prepared at 80°C measured at higher temperatures than 300 K.

Fig. 11. Thermal variation of the superparamagnetic fraction in $CoFe_2O_4$ nanoparticles derived from the Mössbauer spectra.

magnetization since the superparamagnetic relaxation is a dynamic process and the measuring time scales of both methods are completely different. Indeed, Zhang et al. have shown that T_B of some magnetic nanoparticles estimated from temperature-dependent magnetization decay is much lower than that from Mössbauer data [16,17]. However, T_B from a magnetization measurement is strongly dependent upon the applied field and it will shift to higher value under higher magnetic field. The T_B that was estimated from the magnetization decay in field-free condition by Zhang et al. can be therefore different from that estimated from the magnetization maximum which, here we obtained, was measured under the applied magnetic field (100 G). Zhang et al. have also obtained two different T_B values for Co-ferrite nanoparticles with similar sizes of 8.5–9 nm: one was 151 K from magnetization decay [16] and the other was about 300 K from magnetization maximum [4]. The latter is closer to that (394 K) from Mössbauer data [16]. Therefore, the blocking temperatures estimated from magnetization measurement and Mössbauer spectra for the same sample cannot be in principle same due to different time scale if they are measured under the same field-free condition. However, they, estimated from magnetization measurement under an applied field and Mössbauer spectra under field-free condition, can be apparently similar depending on the strength of applied field even though the quantitative prediction may not be possible. In our cases, the T_Bs, measured from both methods, are roughly close together as shown in Table 1.

For the sample B, the Mössbauer spectrum at 125 K shown in Fig. 8 is consisted of mainly a quadrupole doublet with a very small portion of split sextet. It means that most of the particles are superparamagnetic at this temperature. This is consistent with the above argument from the temperature dependence of magnetization for sample B if the blocking temperatures from Mössbauer data and the magnetization measurement are similar to each other as mentioned above. Therefore the average particle size of the sample B is close to that of the sample A despite of some larger particles included in it. Slawska-Waniewska et al. reported that the cobalt ferrite nanoparticles

of 3.3 nm in diameter showed the blocking temperature of 85 K from Mössbauer spectra [18]. This value is roughly consistent with those of the samples A and B estimated from Mössbauer spectra.

4. Conclusion

We have prepared $CoFe_2O_4$ nanoparticles in aqueous solutions at various temperatures by coprecipitation method without any template. The average particle sizes of the ferrites, estimated from XRD line broadening, were 2.0, 2.4, 9.2 and 13.8 nm when the precipitation temperatures are $20°C$, $40°C$, $60°C$ and $80°C$, respectively. As the precipitation temperature increased, the average sizes increased. However, there was a transition in size and crystallinity at the temperature between $40°C$ and $60°C$. The field-dependent and temperature-dependent magnetization measurements and Mössbauer spectra measured at various temperatures showed that the cobalt ferrites nanoparticles prepared at the temperature lower than $40°C$ are entirely superparamagnetic at room temperature with T_B of around 80 K and those, prepared at temperatures higher than $60°C$, consisted of superparamagnetic and ferromagnetic components with T_B higher than 400 K. For the latter, the fraction of superparamagnetic components decreased as the precipitation temperature increased with the increased particle size.

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