Journal of the Korean Chemical Society
2012, *Vol. 56, No. 5*
Printed in the Republic of Korea
http://dx.doi.org/10.5012/jkcs.2012.56.5.609

Characteristics of Barium Hexaferrite Nanoparticles Prepared by Temperature-Controlled Chemical Coprecipitation

Jun Young Kwak, Choong Sub Lee†, Don Kim, and Yeong Il Kim*
*Department of Chemistry, Pukyong National University, Busan 608-737, Korea. *E-mail: ykim@pknu.ac.kr*
†Department of Physics, Pukyong National University, Busan 608-737, Korea
(Received June 29, 2012; Accepted July 24, 2012)

ABSTRACT. Ba-ferrite ($BaFe_{12}O_{19}$) nanoparticles were synthesized by chemical coprecipitation method in an aqueous solution. The particle size and the crystallization temperature of the Ba-ferrite nanoparticles were controlled varying the precipitation temperature. The precipitate that was prepared at 0 °C showed the crystal structure of Ba-ferrite in X-ray diffraction when it was calcined at the temperature above 580 °C, whereas what was prepared at 50 °C showed the crystallinity when it was calcined at the temperature higher than about 700 °C. The particle sizes of the synthesized Ba-ferrite were in a range of about 20-30 nm when it was prepared by being precipitated at 0 °C and calcined at 650 °C. When the precipitation temperature increased, the particle size also increased even at the same calcination temperature. The magnetic properties of the Ba-ferrite nanoparticles were also controlled by the synthetic condition of precipitation and calcination temperature. The coercive force could be appreciably lowered without a loss of saturation magnetization when the Ba-ferrite nanoparticles were prepared by precipitation and calcination both at low temperatures.

Key words: Ba-Ferrite, Magnetic materials, Precipitation, Mössbauer spectroscopy, Magnetic properties

INTRODUCTION

Barrium hexaferrite, $BaO{\cdot}6Fe_2O_3$ of magnetoplumbite type is one of magnetic materials that have been extensively studied since Went et al. first developed.[1] Due to the high magnetic anisotropy, high coercivity, modest magnetic moment and excellent chemical stability, it has been highly concerned for high-density magnetic recording media.[2] Since the traditional high temperature solid state synthesis needs heat treatment at temperature higher than 1200 °C, the synthesized ferrite is inhomogeneous in size and hardly had single magnetic domain. Thus the particles are crushed into smaller particles by milling et al. after synthesis. However, the milled particles are not good in magnetic characteristics because of the lattice strain introduced during milling. Therefore, it is essential to crystallize the ferrite at relatively low temperature in order to get homogeneous particles in size and magnetic properties. There have been developed several synthetic methods for low temperature synthesis such as chemical coprecipitation,[3-7] glass crystallization,[8-10] sol-gel,[11-13] microemulsion,[14] organometallic precursor,[15,16] and hydrothermal methods.[17-19] Among them the chemical coprecipitation method has not been well systematically studied since early studies despite it is most basic and relatively simple procedure. Some reports showed that the magnetic properties and particle sizes of Ba-ferrite prepared by chemical coprecipitation could be controlled by doping some transition metal cations.[20] Previously we reported that Co-ferrite nanoparticles that were prepared by precipitation method in aqueous solution could be varied in size and magnetic properties by controlling simply precipitation temperature.[21] In this study, we have prepared Ba-ferrite nanoparticles by controlling coprecipitation temperature in simple chemical coprecipitation method and investigated the structural and magnetic properties of those Ba-ferrite nanoparticles.

EXPERIMENTAL

Synthesis of Nanoparticle Ba-ferrites

The mixed solution of 0.625 g $BaCl_2{\cdot}2H_2O$ (98.5%, Junsei) and 6.700g $FeCl_3{\cdot}6H_2O$ (98%, Aldrich) in 40 ml of 0.6 M HCl was slowly introduced drop-by-drop into 150 mL of 1.5 M NaOH solution that was previously adjusted to pH 11-12 with conc. HCl. During the addition of the mixed solution, the solution of 1.5 M NaOH was simultaneously added to keep pH 11-12. The temperature of the reaction solution was maintained constant within ±1 °C with a circulating thermostatic bath and the solution was vigorously stirred. The dark brown precipitate immediately appeared as the mixed solution was added and the reac-

tion solution was kept stirred for 30 minutes after the mixed solution was added completely. The precipitate was centrifuged at 7000 rpm for 10 minutes and washed with deionized water. The centrifugation and washing were repeated about 10 times until the washed water was free from Cl^- ions. The washed precipitate was dried under vacuum at an ambient temperature. The dried precipitate was calcined for 4 hours at various temperatures in air to give crystalline Ba-ferrites.

Apparatus

X-ray diffraction patterns (XRD) were obtained with Pillips MAX-2000 X-ray diffractometer with CuKα and 0.02°/sec scan rate. The transmission electron microscope (TEM) images were taken by Jeol JEM-2010 with a carbon-coated copper grid. The temperature-dependent magnetizations were measured with Lakeshore 7000 series ac-magnetosusceptometer at 1 Oe and 1 kHz. The magnetic hysteresis curves were obtained with Lakeshore model 7300 vibrating sample magnetometer. The co-precipitation temperature was controlled with JeioTech RBC-30 refrigerated bath circulator with a mixture of ethylene glycol and water. The data of thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were obtained with Perkin-Elmer TGA7 and DTA7, respectively. The measurements were done under air with the temperature raising rate of 5 °C/min. Mössbauer spectra were collected by Fast Comtec FG-351 spectrometer with ^{57}Co source doped in metallic Rh that was oscillated in a sinusoidal mode.

RESULTS AND DISCUSSION

Figs. 1, 2, and 3 show the XRD patterns of the Ba-ferrites and their precursors that were prepared by precipitation at 0, 30 and 50 °C, respectively and calcination at various temperatures. When the calcination temperature (T_c) was 750 °C, the XRD patterns confirm the structure of barium hexaferrite for all samples irrespective of the precipitation temperature (T_p). When T_c decreased to 650 °C, however, the sample that was precipitated at 50 °C does not show the crystallinity of the ferrite, whereas the samples precipitated at 0 and 30 °C still show the crystal structure of the ferrite. When the temperature further decreased to 600 °C, the sample precipitated at 0 °C show the structural peaks more intense than those of the sample prepared at 30 °C. Therefore, the crystallization temperature of barium hexaferrite depends upon the precipitation temperature of the precursor when it was prepared by the

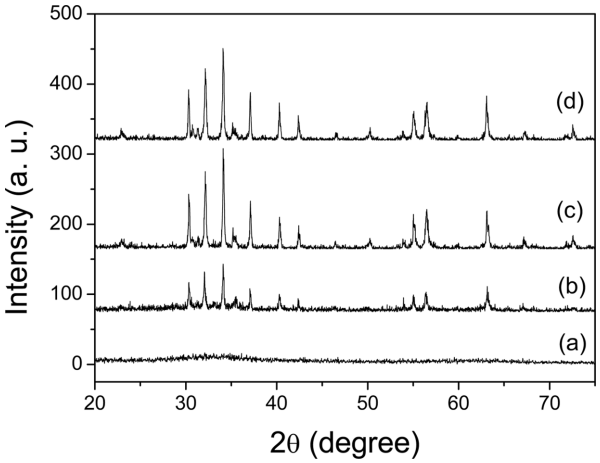

***Fig.* 1.** X-ray diffraction patterns of Ba-ferrites prepared by coprecipitation at 0 °C and calcination at various temperatures: (a) as precipitated, (b) 600 °C, (c) 650 °C, (d) 750 °C.

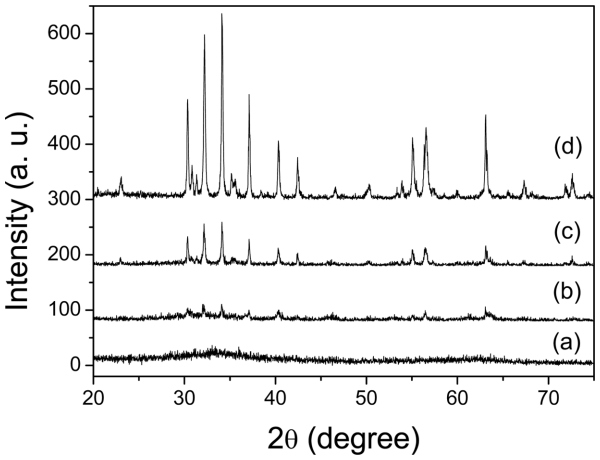

***Fig.* 2.** X-ray diffraction patterns of Ba-ferrites prepared by coprecipitation at 30 °C and calcination at various temperatures: (a) as precipitated, (b) 600 °C, (c) 650 °C (d) 750 °C.

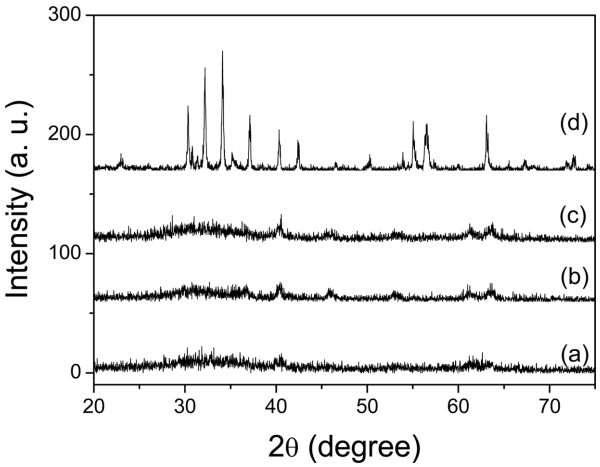

***Fig.* 3.** X-ray diffraction patterns of Ba-ferrites prepared by coprecipitation at 50 °C and calcination at various temperatures: (a) as precipitated, (b) 600 °C, (c) 650 °C (d) 750 °C.

coprecipitation method in basic aqueous solution. The precursors were all apparently amorphous but the precursor prepared at 50 °C shows some small peaks same as the peaks that appeared when it was calcined at 600 and 650 °C. These peaks do not correspond to any crystal structures of the possible intermediates such as α-Fe_3O_4, BaO, $Fe(OH)_3$ and δ-FeOOH. There are not much known detail investigations, as far as we know, for the intermediates when barium hexaferrite was prepared by coprecipitation method. The intermediate was usually assumed or identified to be a hydrated hydroxide or haematite. If we assume that our precursors were in simple hydroxide form, the chemical composition can be written as $BaFe_{12}(OH)_{38}$. When it is calcined to give barium hexaferrite, $BaFe_{12}O_{17}$, the loss of weight is theoretically 23.54%. If the hydroxide is hydrated, the weight loss will be more than this. The weight losses of the precursors prepared here, however, were only about 11-13% as shown in the thermogravimetric analysis (TGA) of *Fig.* 4(a). Moreover, more than 65% of the losses occurred below 250 °C. Since the ferric hydroxide was known to transform to the oxide at the temperature of 250-400 °C,[22] it is hard to say that the precursor is a hydroxide or a hydrated hydroxide. If the weight loss below 250 °C was due to hydrated water and the slow loss after 250 °C was due to the hydroxide, it might be reasonable that the precursors were assumed to have mixed compositions of oxide and hydroxide. Then the plausible chemical formula can be $BaO{\cdot}xFe_2O_3{\cdot}(12\text{-}2x)Fe(OH)_3{\cdot}yH_2O$. If we assume that the initial 7-10% weight loss among the 11-13% loss is due to hydrated water and next 3-4% loss was due to the hydroxide from TGA data in *Fig.* 4(a), x and y will be 5.1-5.4 and 3.9-6.2, respectively. The ratio of hydroxide to oxide per Fe atom is about 0.19-0.12. The precursor prepared at lower temperature has more hydrated water.

The XRD patterns of all samples prepared at three different temperatures did not change and remained amorphous until T_c reached above 550 °C and no haematite phase appeared. If the precipitates were simple mixtures of iron and barium hydroxides, one could expect that haematite phase would appear at about 500 °C. Our result supports that the precipitates were not of a simple hydroxide form. According to the previous studies for the pure Ba-ferrite prepared by chemical co-precipitation method, Haneda et al. showed that the ferrite was crystallized above 800 °C through the intermediate α-Fe_2O_3 at 650 °C.[3] On the other hand, Roos reported the crystallization at 740 °C without any intermediate phase.[4] Shin and Kwan who used the modified co-precipitation method of using Fe^{2+} and H_2O_2 reported that the ferrite was crystallized at the temperature as low as 600 °C through the intermediate α-Fe_2O_3 at 550 °C from initial δ-FeOOH.[23] Our results showed that the crystallization of Ba-ferrite could be occurred without an intermediate crystal phase from mostly amorphous phase of mixed oxide and hydroxide and the crystallization temperature could be lowered if the precipitation temperature is lowered. This point is confirmed from the differential thermal analysis (DTA) data shown in *Fig.* 4(b). The exothermic peaks in the DTA data refer to a phase transition of crystallization process since there is no significant weight change at those temperatures. The data clearly indicates that the crystallization temperature of the precursors prepared at different T_ps systematically increased as T_p increased although the crystallization temperatures do not match with XRD data. The discrepancy between XRD and DTA comes from nonequilibrium process of DTA.

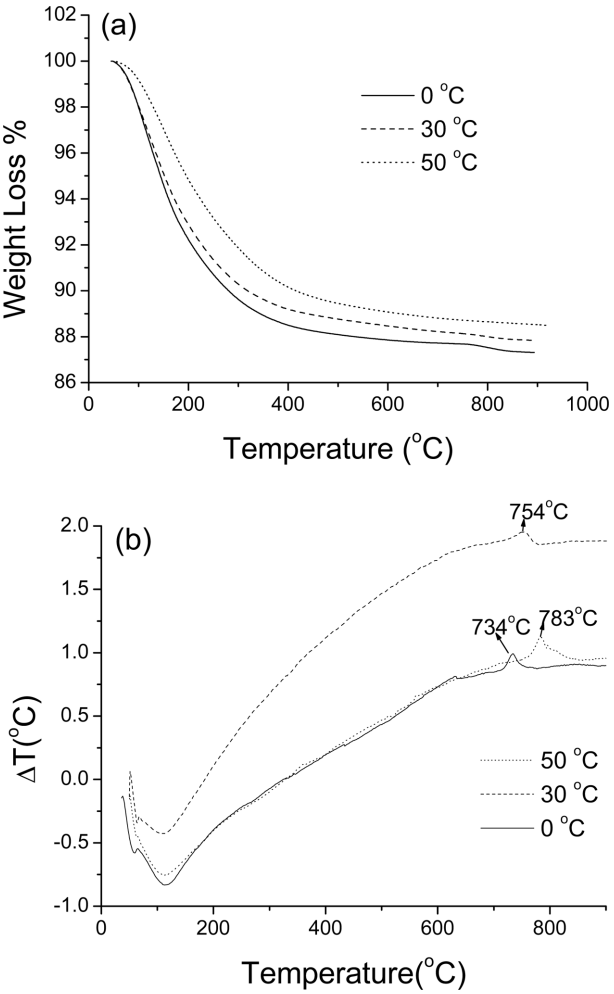

***Fig.* 4.** Thermal gravimetric (a) and differential thermal (b) analyses of the coprecipitates prepared at different temperatures.

***Table* 1.** Unit cell parameters of the synthesized Ba-ferrite nanoparticles

Coprecipitation Temperature (°C)	Calcination Temperature (°C)	*a* (Å)	*c* (Å)	*c/a*
0	600	5.8871	23.288	3.9557
	650	5.8874	23.260	3.9508
	750	5.8903	23.236	3.9447
30	650	5.8866	23.179	3.9375
	750	5.8880	23.191	3.9387
	900	5.8894	23.180	3.9358
50	750	5.8889	23.156	3.9415
	900	5.8923	23.176	3.9333

Since DTA was measured during increasing temperature at a constant rate, the process is not at equilibrium. So the peak position depends on the temperature scan rate. When the scan rate increased, the exothermic peak indeed shifted to high temperature.

The lattice parameters that were obtained from XRD data by nonlinear least square method are summarized in *Table* 1. The parameter *a* and *c* values are in 5.887-5.892, 23.288-23.156, respectively for all samples prepared at T_p of 0-50 °C and T_c of 600-900 °C. As T_c increased, the value of *a* increased while that of *c* decreased. Therefore, the ratio *c*/*a* was systematically decreased and close to the value of the known single crystal Ba-ferrite (*c*/*a*=3.936)[24] as both T_p and T_c increased. The sample that prepared at T_p =0 °C and T_c=600 °C shows an elongated structure in *c*-axis with *c*/*a* value 0.5% higher than the known value. The calculated particle sizes of the ferrite are in the range of 35-50 nm from the Debye-Scherrer equation using the peak of (110) in XRD data. These sizes are coincident with the values from TEM pictures. *Fig*. 5 show the TEM pictures of the ferrite prepared at T_p=0 and 30 °C and T_c= 650 and 750 °C. The particle shapes are mostly round and platelet. The samples prepared at T_c=650 °C showed the sizes of 20-30 and 30-50 nm for T_p=0 and 30 °C, respectively. When the sample prepared at T_p=30 °C were calcined to 750 °C, the particles were fused together and bar-shaped with 50-100 nm size.

Fig. 6 show the room temperature Mössbauer spectra of the samples prepared at T_p=0 and 30 °C and T_c=650 °C. Both of the spectra were deconvoluted to five kinds of sextet peaks that correspond to typical five different kinds of Fe sites in a M-type Ba-ferrite, i.e. three octahedral, one tetrahedral and one trigonal bipyramidal sites.[25] The isomer shifts are 0.284-0.390 and 0.279-0.386 for the samples of T_p=0 and 30 °C, respectively. This means that the oxidation state of all Fe in the ferrite is +3. Therefore, the spectra confirm that all the samples are in single phase of Ba-ferrite. *Fig.* 7 show the Mössbauer spectra of the sample prepared at T_p=0 °C and T_c=600 °C measured at room temperature and 80 K. The spectrum at room temperature consisted of a large quadrupole doublet in the middle and some small split peaks outside. Those small split peaks are hardly fitted to sextet peaks because of too low intensity. Since this sample showed the crystallinity of typical Ba-ferrite in XRD (*Fig.* 1b), the quadrupole doublet repre-

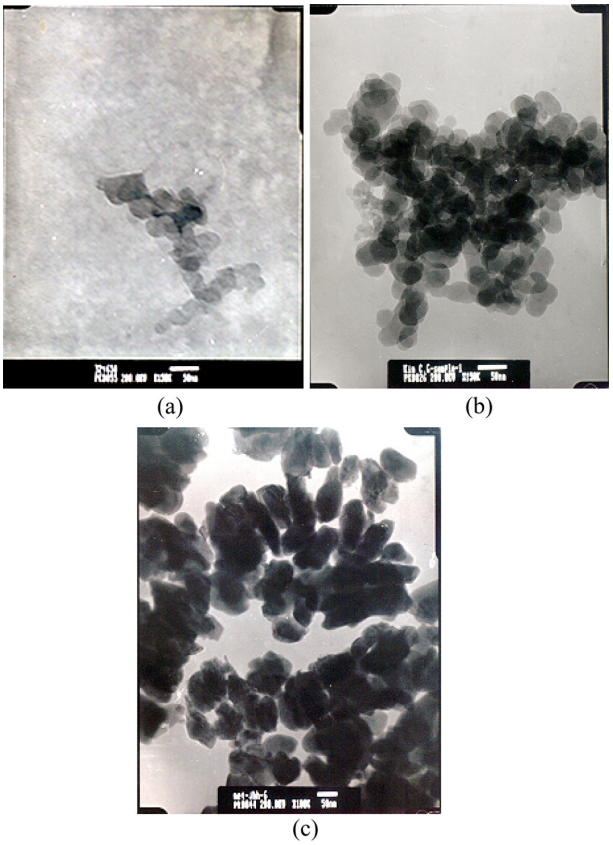

***Fig.* 5.** Transmission electron micrographs of Ba-ferrites prepared by coprecipitation and calcination at (a) 0 °C and 650 °C, respectively; (b) 30 °C and 650 °C; (c) 30 °C and 750 °C. Scale bar indicates 50 nm.

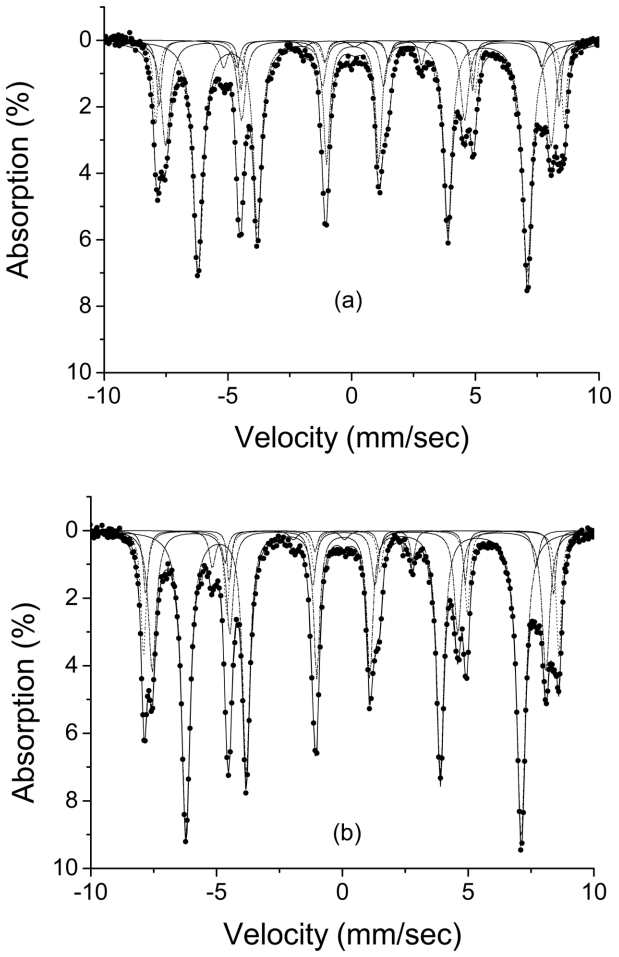

***Fig.* 6.** Mössbauer spectra of Ba-ferrites prepared by coprecipitation at 0 °C(a) and at 30 °C(b) and both calcination at 650 °C. Both spectra were measured at room temperature. Dots are measured values and all other lines are fitted values.

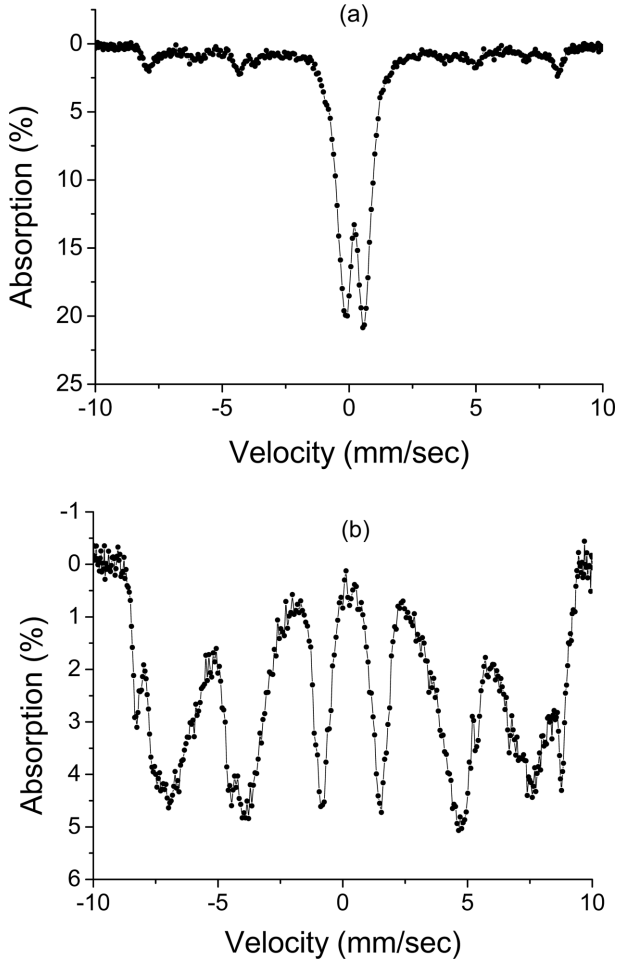

***Fig.* 7.** Mössbauer spectra of Ba-ferrites prepared by coprecipitation at 0 °C and calcination at 650 °C: (a) measured at room temperature, (b) measured at 80 K.

sents the superparamagnetic character of the sample due to the small particles whose Neel temperature (T_N) is below room temperature and the small split peaks are due to the relatively larger particles. When this sample was measured at 80 K, the center quadrupole doublet disappeared and the broad sextet peaks appeared. This result implies that the Neel temperature of this sample may be close to 80 K but the size distribution of the ferrite particles is relatively broad. For the comparison, the Mössbauer spectra of the sample that is precipitated at 0° and not calcined are shown in *Fig.* 8. Both the spectra that measured at room temperature and 80 K consist of quadrupole doublets. Therefore this precursor is composed of all superparamagnetic particles at 80 K as well as at room temperature. The temperature dependence of magnetic susceptibility for the samples prepared at different T_ps is shown in *Fig.* 9. All the uncalcined samples shows maximum magnetization with blocking temperatures, at which the superparamagnetic relaxation starts to appear, below 75 K and the blocking temperature systematically decreased as T_p decreased. This indicates that the particle size of the uncalcined samples also decreases as T_p decreases because the blocking temperature decreases as the particle size decreases. For the sample that was precipitated at 0 °C and calcined at 600 °C, the blocking temperature is around 85 K as shown in *Fig.* 9(c) although it cannot be well defined. This result is coincident with that from Mössbauer data shown in *Fig.* 7.

Fig. 10 shows the magnetic hysteresis curves of the Ba-ferrites that were prepared at different T_ps and T_cs. The magnetization curve does not saturate even at 15 kOe because of the high anisotropic characteristics of Ba-ferrite. So we used the maximum magnetization at the highest applied field herein used (15 kOe) as the saturation magnetization. As shown in the figure, the coercivity (H_c) and saturation

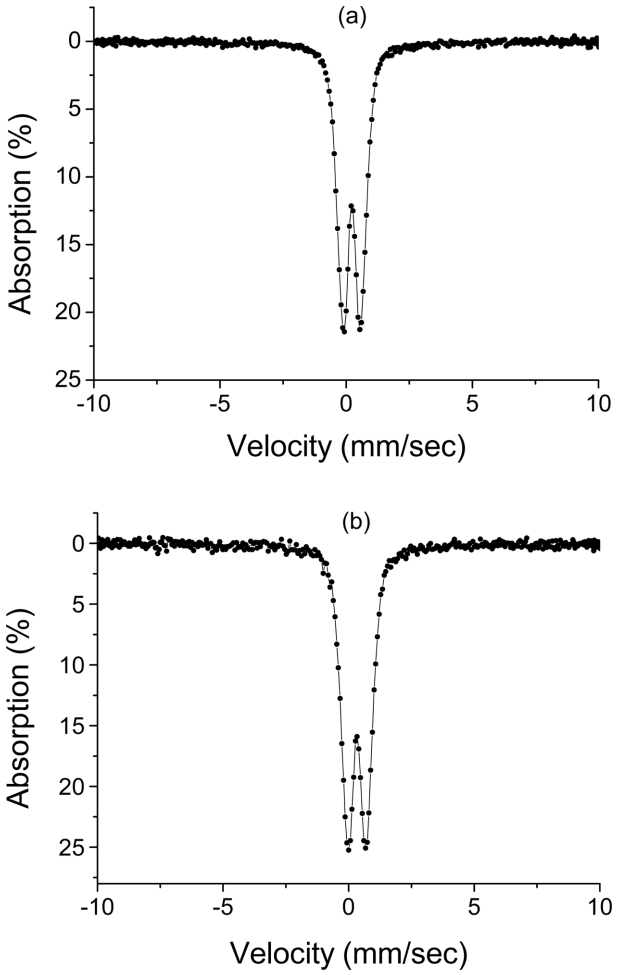

Fig. **8.** Mössbauer spectra of Ba-ferrites prepared by coprecipitation at 0 °C and without calcination: (a) measured at room temperature, (b) measured at 80 K.

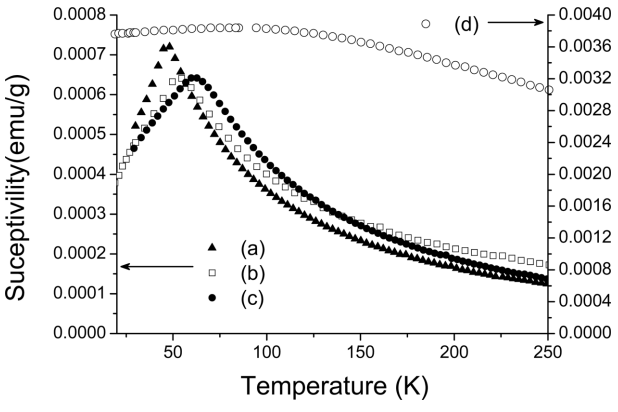

Fig. **9.** Temperature-dependent ac magnetic susceptibility for Ba ferrite prepared by coprecipitation at 0 (a), 30 (b) and 50 °C (c) without calcination and with calcination at 600 °C (d).

magnetization (M_s) are appreciably different for the samples prepared at the different precipitation temperatures

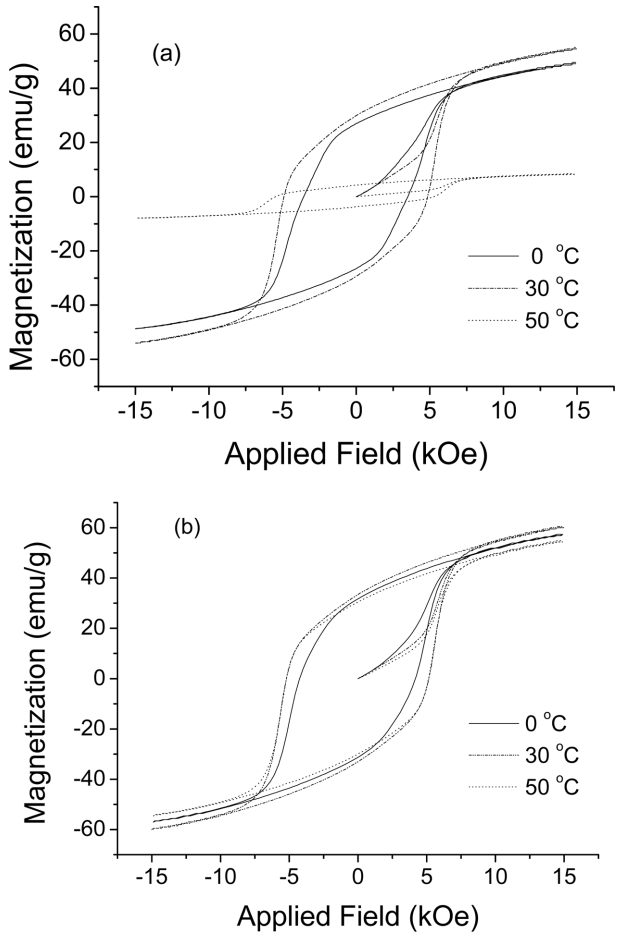

Fig. **10.** Magetization vs. applied magnetic field for Ba-ferrites prepared by coprecipitation at various temperatures and calcination at 650 °C (a) and 750 °C (b) (measured at room temperature).

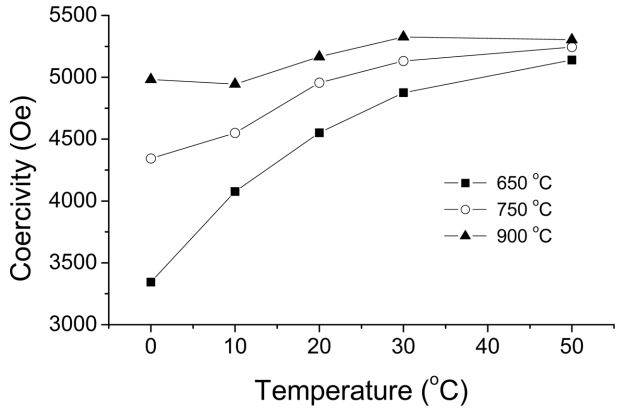

Fig. **11.** Coercivity vs. coprecipitation temperature for Ba-ferrites prepared by coprecipitation and calcination at various temperatures.

when the calcination temperature was 650 °C. When the calcination temperature became higher, the difference in H_c and M_s became smaller. The precipitation temperature dependence of H_c and M_s for the samples prepared at dif-

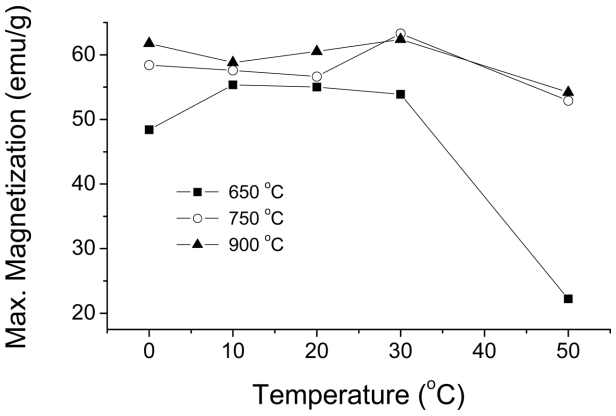

***Fig*. 12.** Saturation magnetization vs. coprecipitation temperature for Ba-ferrites prepared by coprecipitation and calcination at various temperatures.

ferent calcination temperatures are plotted in *Fig*. 11 and 12. The coercivity increased generally as T_p increased regardless of T_c. The coercivity change by increasing calcination temperature is larger for the sample prepared at lower T_p. While the coercivity change of the sample prepared at T_p = 0 °C is 1.8 kOe when T_c increased from 650 to 900 °C, that for the sample prepared at T_p=50 °C was only 0.3 kOe at the same T_c change. On the other hand, the saturation magnetization was not very dependent on the precipitation temperature except the sample of high precipitation and low calcination temperatures. For the sample prepared at T_p=50 °C the M_s changed from 22 to 54 emu/g when T_c increased from 650 to 900 °C. Therefore, the coercivity of the ferrite could be lowered without the loss of saturation magnetization when it was prepared at low T_p and T_c.

CONCLUSION

In this study, we have shown, for the first of time as far as we know, that the crystallization temperature of Ba-hexaferrite nanoparticles could be varied according to the precipitation temperature (T_p) of the precursors when the ferrite were prepared by a simple chemical precipitation method. When T_p was 0 °C, the crystallinity in XRD appeared at the calcination temperature (T_c) lower than 600 °C. Whereas, T_p was 50 °C, the crystallinity did not appear even at 650 °C. The precipitation precursors were inferred to be mostly in oxide form rather than in hydroxide form to be thought previously. We could synthesize relatively smaller size of Ba-ferrite than previously reported as 20-30 nm in its diameter when it was prepared at T_p=0 °C and T_c=650 °C. The magnetic properties of those Ba-ferrite nanoparticles could be varied depending on T_p and T_c. Especially, the magnetic coercivity strongly depended on the calcination temperature when the precursor was prepared at low T_p while there was no such dependence for the precursor prepared at high T_p. Therefore the coercivity of Ba-ferrite could be lowered without loss of saturation magnetization when the ferrite was prepared at low T_p and T_c. This implies that the drawback of too high coercivity in Ba-ferrite can be complimented by controlling the synthetic condition when the ferrite was applied to various magnetic devices.

Acknowledgments. This work was supported by Korean Ministry of Education through Research Fund (BSRI-98-2455).

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