

Preparation and Magnetic Properties of BaFe₁₂O₁₉ Particles Coated with Epitaxially Grown Fe₃O₄ Layers: 6xFe₃O₄(1 - x)BaFe₁₂O₁₉

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Platelike particles of BaFe₁₂O₁₉ with epitaxially grown Fe₃O₄ overlayers, 6xFe₃O₄(1 - x)BaFe₁₂O₁₉, were prepared by a wet method. The structure was characterized by X-ray diffraction and TEM and SEM observations. Magnetic properties were studied by VSM and Mössbauer spectroscopic measurements. In order to study the magnetic behavior of very thin Fe₃O₄ overlayers, Mössbauer measurements were applied to enrich samples, 6x⁵⁷Fe⁵⁶Fe₂O₄(1 - x)Ba⁵⁶Fe₁₂O₁₉, prepared from alkaline suspensions of Ba⁵⁶Fe₁₂O₁₉ particles and ⁵⁷Fe(OH)₂. © 1992 Academic Press, Inc.

1. Introduction

Hexagonal platelike particles of barium ferrite, BaFe₁₂O₁₉, have attracted renewed attention as a candidate for perpendicular magnetic recording material. For the purpose to reduce the too-high coercive force, *H_c*, a partial substitution of Fe³⁺ with a Co²⁺ + Ti⁴⁺ pair was attempted. However, not only the decrease of *H_c* but also the reduction of magnetization, *M*, has resulted (1). If the surfaces of BaFe₁₂O₁₉ particles are able to be coated with Fe₃O₄ layers, an increase in *M* seems to be possible simultaneously with the decrease in *H_c*. The present authors succeeded in preparing BaFe₁₂O₁₉ particles coated with epitaxially grown Fe₃O₄ layers by aging platelike particles of BaFe₁₂O₁₉ in the presence of Fe(OH)₂

in N₂. The experimental results on the preparation, characterization, and magnetic measurements are presented in this paper. For Mössbauer spectroscopic measurements specifically to study the Fe₃O₄ layers, ⁵⁷Fe-enriched samples were prepared. On the surface of BaFe₁₂O₁₉ particles composed of only ⁵⁶Fe³⁺, the enriched Fe₃O₄ layer coating was carried out by using ⁵⁷Fe(OH)₂. Thus, the Mössbauer spectra exclusively represent the behaviors of very thin Fe₃O₄ layers on BaFe₁₂O₁₉ particles.

2. Experimental

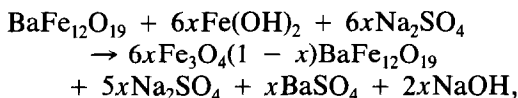
Platelike particles of BaFe₁₂O₁₉ with the BET surface area, *S*, of 7 m²/g were prepared by a procedure similar to the one previously described (2). A suspension, containing 0.092 M Ba(II), 0.734 M Fe³⁺ and 6 M excess NaOH, was subjected to autoclaving at 300°C for 5 hr. The resulting precipitate was well washed with water and separated by filtration. The filtrated precipitate, containing 53.5 wt% of BaFe₁₂O₁₉ was

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stored in a polyethylene container. A part of the precipitate was dried in air at 100°C to apply physical measurements.

Suspensions of 30 ml including 3.6 mmol $\text{BaFe}_{12}\text{O}_{19}$ and different amounts of NaOH and FeSO_4 , in 60 ml tetrafluoroethylene bottles were stirred ultrasonically for 15 min and diluted with water up to 50 ml. The sample formation in the absence of excess NaOH in the starting suspension, $\text{BaFe}_{12}\text{O}_{19} + 6x\text{FeSO}_4 + 12x\text{NaOH}$, is expressed as



where H_2O molecules are abbreviated.

The bottle containing the suspension was stoppered by a tetrafluoroethylene cap in N_2 and was subjected to aging at temperatures between 50 and 100°C for 5 hr. During the course of aging, the suspension was vigorously shaken up for 1 min at every hour. The pH of the suspension subjected to aging was decreased to 4 at room temperature with the addition of 1 M HCl to remove the remaining $\text{Fe}(\text{OH})_2$ and then each black, ferromagnetic precipitate in the acidic suspension was separated by filtration, well washed with water, treated with acetone, and dried at 40°C. The content of Fe^{2+} in the acidic filtrate, separated from the acidic

suspension, was estimated by means of $\text{K}_2\text{Cr}_2\text{O}_7$ titration. The BaSO_4 content in the sample was measured by gravimetric analysis, after it had been dissolved into HCl by heating.

In order to characterize the obtained samples, X-ray diffraction (XRD), transmission and scanning electron microscope (TEM and SEM), magnetic measurements up to 10 kOe at room temperature by a vibrating sample magnetometer (VSM), and Mössbauer spectroscopic measurements were applied.

The relative contents of Fe_3O_4 in each sample, were estimated from the content of BaSO_4 , and the difference in M , before and after aging, by assuming that the M -values at 10 kOe of $\text{BaFe}_{12}\text{O}_{19}$ and Fe_3O_4 are 48.3 and 84.7 emu/g, respectively (see Table II). The Fe_3O_4 content was also estimated by comparing the relative intensities of XRD peaks of $\text{Fe}_3\text{O}_4(d(311) = 2.532 \text{ \AA})$, $\text{BaFe}_{12}\text{O}_{19}(d(107) = 2.77 \text{ \AA})$, and $\text{BaSO}_4(d(210) = 3.319 \text{ \AA})$.

The $\text{Ba}^{56}\text{Fe}_{12}\text{O}_{19}$ sample with $5 \text{ m}^2 \text{ g}^{-1}$ in S , consisting only of hexagonal, platelike particles, was prepared under conditions similar to those for the $\text{BaFe}_{12}\text{O}_{19}$ preparation above mentioned by using an acidic solution of $^{56}\text{Fe}^{3+}$ (99%) prepared by dissolving $^{56}\text{Fe}_2\text{O}_3$ into HCl solution. The $6x^{57}\text{Fe}^{56}\text{Fe}_2\text{O}_4(1-x)\text{Ba}^{56}\text{Fe}_{12}\text{O}_{19}$ samples

TABLE I

PREPARATION CONDITIONS, COMPOSITIONS, X , AND MAGNETIC PROPERTIES OF SEVERAL $X\text{BaSO}_4 + 6X\text{Fe}_3\text{O}_4(1-X)\text{BaFe}_{12}\text{O}_{19}$ SAMPLES PREPARED BY AGING THE SUSPENSIONS OF $\text{BaFe}_{12}\text{O}_{19} + 6X\text{Fe}(\text{OH})_2$ WITH $X = 1/3$

Sample	Excess NaOH (M)	T (°C)	M (emu/g)	H_c (Oe)	Fe^{2+} (mmol) ^a	BaSO_4 (wt%)	X_1	X_2	X_3
A	0	100	54.7	550	—	4.3	0.22	0.20	0.19
B	0.9	100	57.4	550	0.2	4.6	0.24	0.27	0.29
C	2	100	57.6	590	0.2	4.8	0.25	0.31	0.30
D	2	70	56.9	650	1.1	3.4	0.18	0.20	0.26
E	2	50	52.9	720	2.3	2.9	0.15	0.15	0.14

Note. X_1 , X_2 and X_3 are the values estimated from the BaSO_4 content, XRD peaks, and the difference in M , respectively.

^a Fe^{2+} in filtrate.

were prepared without the process of an acidic treatment (decreased to pH = 4) by using an acidic solution prepared in nitrogen by dissolving ⁵⁷Fe metal(95%) into HCl solution.

3. Results and Discussion

The basic BaFe₁₂O₁₉ particles have a platelike shape with a typical size of 1 μm in diameter and 0.06 μm in thickness. Alkaline suspensions containing Fe²⁺ and BaFe₁₂O₁₉ particles were subjected to aging at temperatures between 50 and 100°C and, then ferromagnetic, brownish or black precipitates consisting of 6xFe₃O₄(1 - x)BaFe₁₂O₁₉ and small amounts of BaSO₄ were formed. In Table I, several examples of obtained samples from the starting suspensions, containing 0.144 M Fe²⁺ and 0.864 M Fe³⁺ (corresponding to 72 mM BaFe₁₂O₁₉) and different concentrations of excess NaOH, are listed. The composition, *x*, of the products becomes greater with the increases in excess NaOH concentration and temperature, reaching near 1/3 in *x* of the starting suspensions. The properties of samples obtained at 100°C with varying the Fe²⁺ concentration at 2 M excess NaOH are given in Table II, together with the starting material, *x* = 0. Figures 1 and 2 show the XRD patterns and SEM photographs for three typical

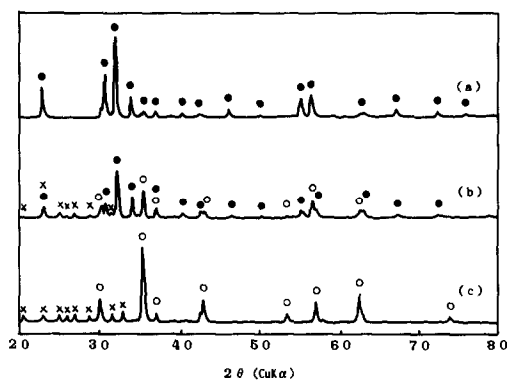


FIG. 1. XRD patterns of 6XFe₃O₄(1 - X)BaFe₁₂O₁₉ samples: (a) sample F, (b) sample C, and (c) sample H. ●, BaFe₁₂O₁₉; ○, Fe₃O₄; ×, BaSO₄.

samples. The XRD pattern changes from that of BaFe₁₂O₁₉ to that of Fe₃O₄ (a slight amount of BaSO₄ in addition), with the increase in *x* to 1.0. On the other hand, the shape of each particle in the samples remains nearly as the original one, regardless of the compositional change.

Figure 3 shows an electron diffraction (ED) pattern together with an example of TEM picture, which was taken for a sample with a smaller particle size for the convenience of electron transmission. Lattice fringes of BaFe₁₂O₁₉ (*d*(002) = 1.1 nm) and Fe₃O₄ (*d*(111) = 0.5 nm) are very clearly observed, which indicate that the Fe₃O₄ lay-

TABLE II

ESTIMATED COMPOSITIONS, *X*, OF THE XBaSO₄ + 6XFe₃O₄(1 - X)BaFe₁₂O₁₉ SAMPLES PREPARED AT 100°C FOR 5 hr FROM SUSPENSIONS CONTAINING 72 mM BaFe₁₂O₁₉(F), 2 M EXCESS NaOH, AND 0.072(G) AND 0.43 M Fe²⁺(H).

Sample	<i>M</i> (emu/g)	<i>H_c</i> (Oe)	BaSO ₄ (wt%)	<i>X</i> ₁	<i>X</i> ₂	<i>X</i> ₃
F	48.3	1100	0	0	0	0
G	53.0	780	2.7	0.13	0.16	0.16
H	71.7 ^a	230	12.6	0.84	1	0.96
I ^b	85.3	190	0	—	1.00	1.00

^a Increases to 72.7 if prepared in the presence of 0.5 M Fe(II).

^b Prepared in the presence of 0.6 M FeCl₂ in place of the sulfate.

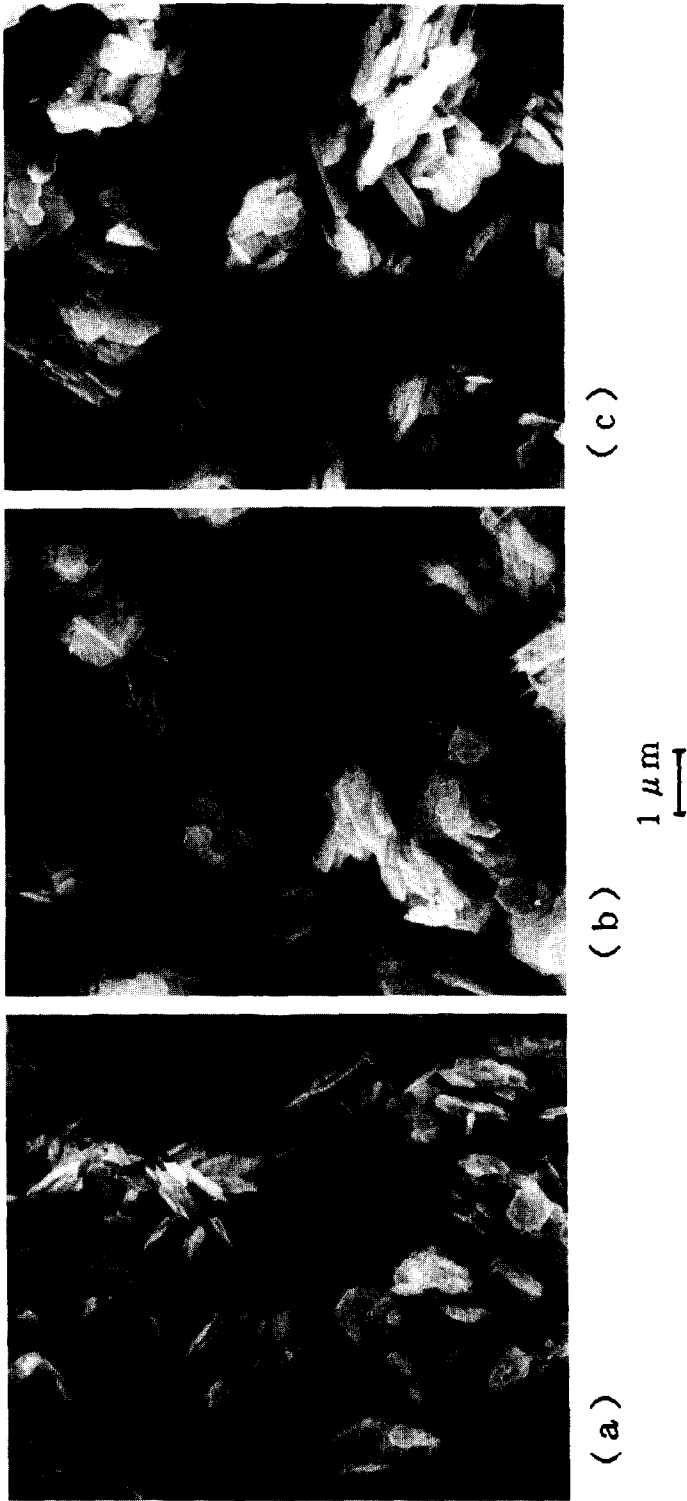


FIG. 2. SEM photographs of $6X\text{Fe}_3\text{O}_4(1-X)\text{BaFe}_{12}\text{O}_{19}$. (a) sample F, (b) sample C, and (c) sample H.

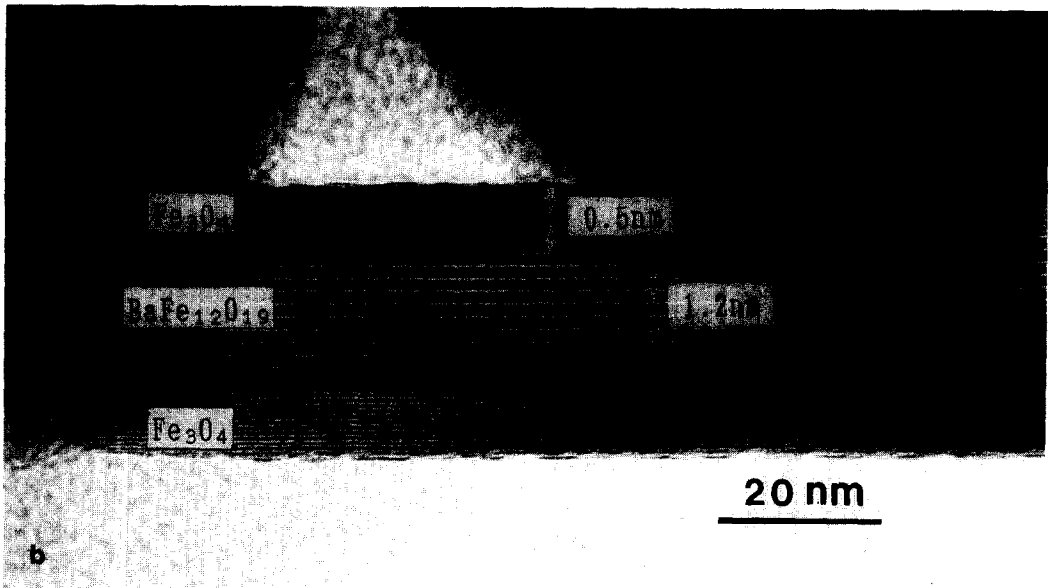
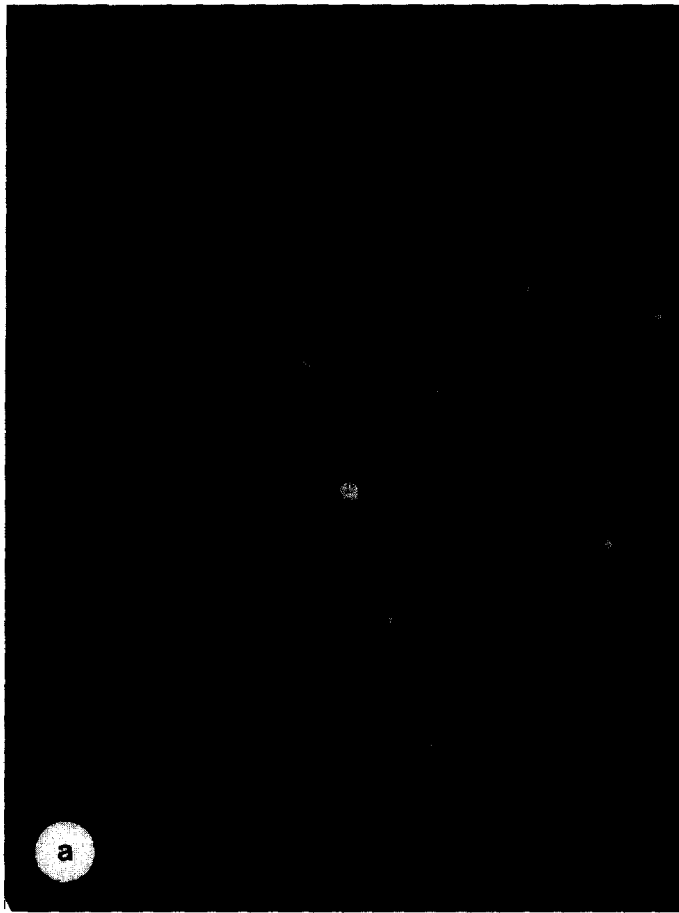


FIG. 3. (a) ED pattern of $6X\text{Fe}_3\text{O}_4(1-X)\text{BaFe}_{12}\text{O}_{14}$ with $X = 1/3$. The electron beam is along the normal of the sample plane. (b) TEM photograph of $6X\text{Fe}_3\text{O}_4(1-X)\text{BaFe}_{12}\text{O}_{14}$ with $X = 1/3$ with the electron beam parallel to the sample plane. The sample for TEM measurement was prepared from a starting $\text{BaFe}_{12}\text{O}_{19}$ particles with smaller size ($0.1 \mu\text{m}$ in diameter) under the same condition with sample C.

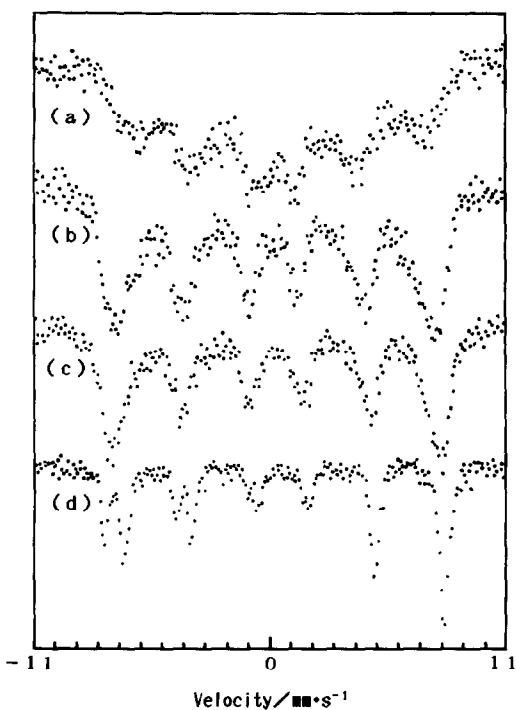


FIG. 4. Mössbauer absorption spectra at 300 K of $^{57}\text{Fe}^{56}\text{Fe}_2\text{O}_4$ layers grown on $\text{Ba}^{56}\text{Fe}_{12}\text{O}_{19}$ particles with different thicknesses: (a) 1, (b) 2, (c) 4 unit cells, and (d) Fe_3O_4 .

ers were grown epitaxially on the surface of $\text{BaFe}_{12}\text{O}_{19}$ particle and Fe_3O_4 (111) planes are parallel to $\text{BaFe}_{12}\text{O}_{19}$ (001). The very sharp interface evidences that the growth of Fe_3O_4 is in a layer-by-layer fashion.

Mössbauer absorption spectra for enriched samples, prepared by aging at 100°C the suspensions containing 2 M excess NaOH , $\text{Ba}^{56}\text{Fe}_{12}\text{O}_{19}$ (with 1160 Oe in H_c and 45.9 emu g^{-1} in M), and slight amounts of $^{57}\text{Fe}(\text{OH})_2$ (with 0.01, 0.02, and 0.04 in the $^{57}\text{Fe}^{56}\text{Fe}$ ratio) are shown in Fig. 4. The thickness of $^{57}\text{Fe}^{56}\text{Fe}_2\text{O}_4$ layer with ^{57}Fe enrichment is hereafter expressed as the number of nominal $^{57}\text{Fe}^{56}\text{Fe}_2\text{O}_4$ unit cells. H_c and M for 2 unit-cell and 4 unit-cell samples are 1100 Oe, 45.9 emu g^{-1} and 1063 Oe, 46.7 emu g^{-1} , respectively. Figure 4 shows the spectra at room temperature for the samples

whose $^{57}\text{Fe}^{56}\text{Fe}_2\text{O}_4$ layer thicknesses with ^{57}Fe enrichment were 1, 2, and 4 unit cells. The spectrum for the sample completely converted into Fe_3O_4 , with keeping the hexagonal platelike particle shape, is also shown for comparison, which is almost identical to that of Fe_3O_4 in the literature (3). All the spectra for the surface $^{57}\text{Fe}^{56}\text{Fe}_2\text{O}_4$ layers consist of ferromagnetic six-line patterns. The spectrum for the 1-unit-cell sample is especially broad because the hyperfine field of the topmost atom layer is smaller than the bulk and perhaps because of quadrupole interaction (4). The spectra for 2- and 4-unit-cell samples also are fairly broad, and the Fe^{3+} contribution seems to be much more dominant than the Fe^{2+} contribution in the spectra. This is due to the oxidation of the sample surface. For the Mössbauer measurements, dried samples were prepared in N_2 but the surface layers were oxidized because of short time contact with air. This result therefore does not mean that the very thin Fe_3O_4 is nonstoichiometric but the surface of present Mössbauer samples is in an intermediate state between Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$.

The Mössbauer absorption spectra for the 2-unit-cell sample were measured in nitrogen at various temperatures and in Fig. 5, the mean hyperfine field is plotted as a function of temperature. The intrinsic Curie temperatures of Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ are 585 and

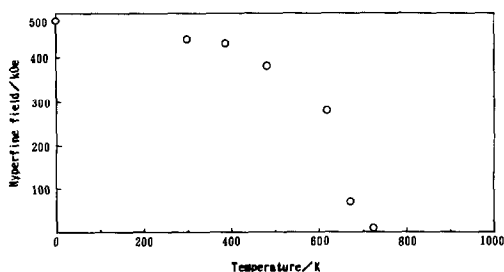


FIG. 5. Temperature dependence of hyperfine field in $^{57}\text{Fe}^{56}\text{Fe}_2\text{O}_4$ layers on $\text{Ba}^{56}\text{Fe}_{12}\text{O}_{19}$ particles with the thickness of 2 unit cells.

675°C, respectively, which are higher than that of BaFe₁₂O₁₉, 450°C (1). However, the temperature where the magnetic hyperfine structure collapses is not the Curie temperature of Fe₃O₄ or γ -Fe₂O₃, but is that of BaFe₁₂O₁₉. Since the overlayers of spinel ferrite are very thin, they are superparamagnetic if the BaFe₁₂O₁₉ matrix is paramagnetic. This result also is an evidence that Fe₃O₄ layers are epitaxially grown on BaFe₁₂O₁₉ particles and magnetically coupled with each other.

The present results indicate that the Fe²⁺, being in equilibrium with a precipitate of Fe(OH)₂, reacts with the Fe³⁺ on the surfaces of hexagonal platelike particles to form the Fe₃O₄ layers on the subsurfaces. The growth of the Fe₃O₄ layers is considered to be assisted by electron transfer through the interface into the particle. By adsorption of the Fe²⁺ on the (001) surface in the crystal structure of BaFe₁₂O₁₉, the Fe₃O₄ layers grow epitaxially on the surface with reduction of the Fe³⁺ in the interior and dissolu-

tion of Ba(II). (How Ba(II) dissolves is not understood presently).

In conclusion, the authors have succeeded in preparing epitaxially layer-by-layer grown Fe₃O₄ layers on the surface of BaFe₁₂O₁₉ particles.

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