Conditions for the Formation of Compounds Consisting of BaO and Fe_2O_3 from Aqueous Suspensions

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Suspensions containing either iron(III) hydroxide or hydroxide oxide and barium ions were subjected to autoclaving at various temperatures from 100 to 300 °C, and the properties of the resulting products were studied. A ferromagnetic precipitate, $BaO \cdot 6Fe_2O_3$, consisting of hexagonal plate-like particles, was obtained by suitable combination of temperature, kind and particle size of iron(III) hydroxide oxide, and concentration of $Ba(OH)_2$. Nonferromagnetic precipitates, $BaO \cdot 4.5Fe_2O_3$ and $BaO \cdot 2Fe_2O_3$, were also formed depending on the conditions. The mechanism of their formation is discussed. The magnetic properties of the $BaO \cdot 6Fe_2O_3$ precipitates are investigated.

$BaO \cdot 6Fe_2O_3$ is widely used as a permanent magnet, and its properties have been thoroughly investigated.[1] The compound can be obtained as a polycrystalline substance when a mixture of iron(III) oxide and barium carbonate is ignited at high temperatures (>800 °C) in an oxidizing gas.[2] The hydrothermal synthesis of $BaO \cdot 6Fe_2O_3$ was achieved for the first time in 1969.[3] It was found that iron(III) hydroxide or hydroxide oxide can react with the barium ion in a suspension to form $BaO \cdot 6Fe_2O_3$ if we choose the proper pH, concentration of barium ion, and temperature; nonferromagnetic precipitates, $BaO \cdot 4.5Fe_2O_3$ and $BaO \cdot 2Fe_2O_3$, are also obtained depending on the conditions.[3]

This paper will deal with the conditions for the formation of compounds consisting of BaO and Fe_2O_3 and with the magnetic properties of $BaO \cdot 6Fe_2O_3$.

Experimental

Material. Chemicals of an analytical grade were used except for the iron(III) hydroxide oxides and oxide. α- and γ-FeO(OH), consisting of needle-like particles of different mean sizes, were prepared by the seed method. Acidic suspensions of very fine, needle-like particles of α- and γ-FeO(OH) (used as seeds) were obtained by the air oxidation of $Fe(OH)_2$ at 40 °C in a $FeSO_4$ solution and of $Fe(OH)_2$ at 15 °C in a $FeCl_2$ solution respectively.[4] A 20-g of iron powder (size<140 μm) was added to 1 l of the suspension. Oxidation to α-FeO(OH) was carried out at 70 °C and to γ-FeO(OH) at 50 °C by bubbling air into the suspension at the rate of 500 l/h.[5] In order to obtain α- and γ-FeO(OH) with different mean particle sizes, the particle growth of FeO(OH) in suspension was controlled by the amount of seed added.

β-FeO(OH), consisting of needle-like particles, was prepared by the air oxidation of mixtures of $FeCl_2$, $FeCl_3$ and NH_4Cl solutions at 70 °C with different concentrations with respect to the total amount of iron.[6] The mean particle size increased with an increase in the concentration.

Needle-like particles, each consisting of very fine particles of α-Fe_2O_3, were prepared by the calcination of α-FeO(OH) particles in air at 300 °C for 2 h.

Procedure. Suspensions containing barium ions and one of iron(III) hydroxide, hydroxide oxide, or oxide were prepared as follows: (1) An acidic solution was prepared in a cylindrical tetrafluoethylene bottle (40 ml) by mixing 12.8 mmol of iron(III) nitrate and 1.6 mmol of barium nitrate in 10—15 ml of conductivity water. To the acidic solution the required amount of NaOH was added in various mol ratios of NaOH to the total nitrate. Water was then added to make the total volume 25.0 ml. (2) Starting suspensions containing either iron(III) hydroxide oxide or oxide, and $Ba(OH)_2$ were also prepared in the cylindrical bottles by mixing 36.0 mmol of iron(III) hydroxide oxide or 18.0 mmol of oxide, and different amounts of $Ba(OH)_2 8H_2O$ in 25.0 ml of water.

In order to prevent carbonation, the preparation was carried out in a nitrogen atmosphere. The bottles containing the suspensions were stoppered with tetrafluoethylene caps and dipped in water contained in an autoclave* to prevent the reduction of the volume of the suspension during the course of autoclaving. Four suspensions were subjected to autoclaving in each run. The suspensions were heated to the desired temperature at the rate of 4 °C/min, and then kept at this temperature for 5 h.

The products were separated from the solution by filtration, treated with a dilute $HClO_4$ solution to remove the remaining $Ba(OH)_2$, washed thoroughly with water, treated with acetone, and dried at 80 °C.

Examination. The products and the iron(III) hydroxide oxides used as the starting materials were examined by means of X-ray powder diffraction using Mn filtered Fe*K*α radiation. The products and the iron(III) hydroxide oxides which were found to consist of only one phase were subjected to BET surface measurements and to optical or electron microscopic observation. Products consisting of only one phase were further washed with 3M-$HClO_4$ to remove the adsorbed barium ion. After they had been dissolved in a HCl solution by heating, the barium and iron(III) ion contents were determined by means of gravimetric analysis.

Results and Discussion

Conditions for the Formation of $BaO \cdot 6Fe_2O_3$. A brown precipitate was formed when the NaOH solution was added to an acidic solution containing iron(III) and barium nitrates. When the NaOH/total NO_3^- in mol ratio ($=R$) was 0.8, most of the iron(III) ions precipitated, the pH of the resulting suspension becoming 2.4—2.8. When $R \geqq 0.9$, the pH of suspensions became > 7 as a result of the formation of $Ba(OH)_2$ (no precipitation). By autoclaving, it turned out that pH≧11 for the suspensions with $R \geqq 0.9$ and pH≦1.1 for those with $R=0.8$.

The formation of the products is shown in Fig. 1 in terms of R and temperature. The concentration of

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* Constructed of stainless steel.

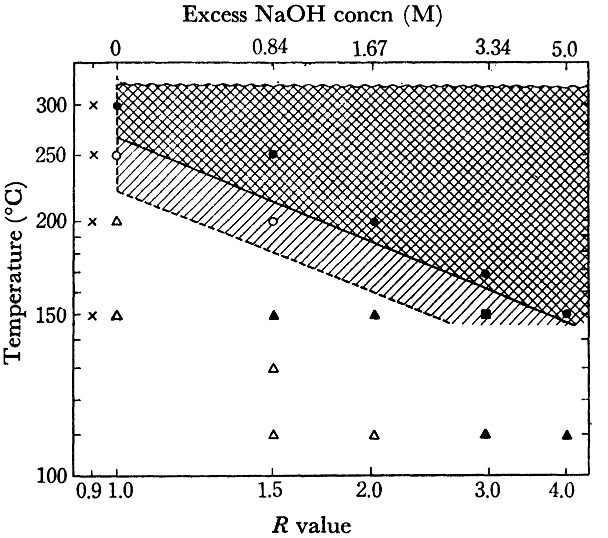


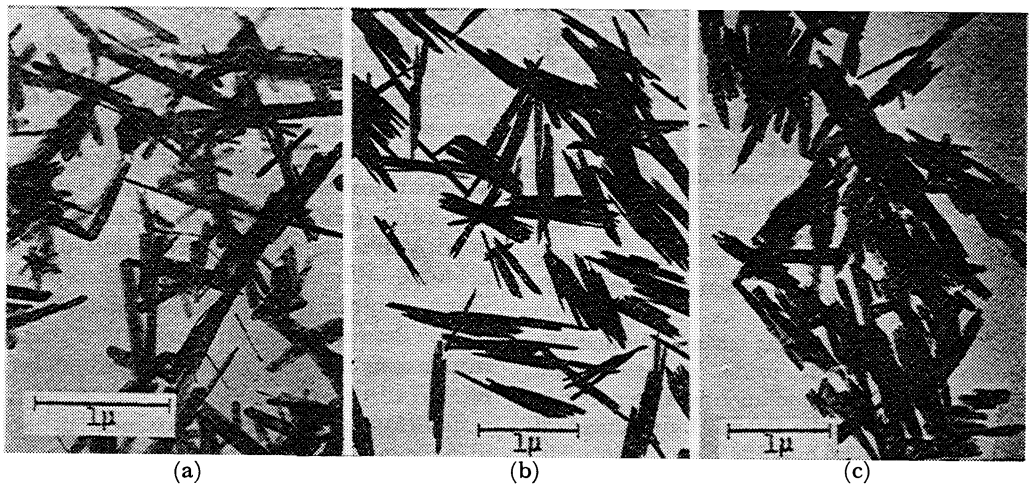
Fig. 1. Conditions for the formation of BaO·6Fe$_2$O$_3$ from suspensions containing 0.514 M-Fe(NO$_3$)$_3$, 0.064 M-Ba(NO$_3$)$_2$, and vairous amounts of NaOH. ● BaO·6Fe$_2$O$_3$, ○ BaO·6Fe$_2$O$_3$+α-Fe$_2$O$_3$, ▲ BaO·4.5Fe$_2$O$_3$, ■ BaO·6Fe$_2$O$_3$+BaO·4.5Fe$_2$O$_3$, × α-Fe$_2$O$_3$, △ BaO·4.5Fe$_2$O$_3$+α-Fe$_2$O$_3$.

excess NaOH in the suspension, as calculated from the *R* value, is also given. BaO·6Fe$_2$O$_3$, a brown ferromagnetic precipitate, is formed in the range of $R>1.0$ at temperatures higher than those for the formation of BaO·4.5Fe$_2$O$_3$, a brown nonferromagnetic precipitate, or a mixture of α-Fe$_2$O$_3$ and BaO·4.5Fe$_2$O$_3$. The temperature at which BaO·6Fe$_2$O$_3$ is formed decreases with the increase in *R*. When similar experiments were carried out with chlorides in place of nitrates, no remarkable difference were found in the conditions for the formation of BaO·6Fe$_2$O$_3$.

The physical and chemical properties of iron(III) hydroxide, formed by the addition of an alkaline solution to an iron(III) salt solution, were studied in detail by van der Giessen.[7] The precipitate consists of superfine particles (30—40 Å in size) stable in a neutral suspension medium. In an alkaline medium, however, the precipitate is transformed into α-FeO(OH) or α-Fe$_2$O$_3$, or their mixture, depending on the temperature of aging.[8–10] α-Fe$_2$O$_3$ is formed at temperatures higher than those at which α-FeO(OH) is formed. The temperature at which α-Fe$_2$O$_3$ is formed depends on the time elapsed during the course of aging at room temperature and on the concentration of the excess alkali. It seems that BaO·6Fe$_2$O$_3$ is formed at such temperatures that iron(III) hydroxide is transformed into α-Fe$_2$O$_3$, provided that the amount of Ba(OH)$_2$ in the suspension is suitable for BaO·6Fe$_2$O$_3$ formation. The content of barium ions in the product increases with the decrease in the solubility of Ba(OH)$_2$ at a given concentration of the total barium ions. The solubility might decrease with a rise in the temperature and with an increase in the NaOH concentration.[11]

Iron(III) hydroxide oxides in alkaline suspension media can be transformed into α-Fe$_2$O$_3$ by autoclaving, the rate of transformation depending on the crystal structure of the iron(III) hydroxide oxides as well as on the particle size and shape. In order to examine the effects of the modification and particle size of iron(III) hydroxide oxide on the formation of BaO·6Fe$_2$O$_3$ in the presence of Ba(OH)$_2$, the following experiments were carried out by the use of iron(III) hydroxide oxides and oxide, similar in particle shape and size (Fig. 2). The suspensions containing 4.5 mmol of Ba(OH)$_2$ and either iron(III) hydroxide oxide or oxide were subjected to autoclaving at 150, 200, 250, and 300 °C. The products are given in Table 1, together with the BET surface area, *S*, of the starting material. We see that the temperature required for the transformation of α-, β-, and γ-FeO(OH) into α-Fe$_2$O$_3$ decreases in this order, and that the use of α-FeO(OH) at higher temperatures favors the formation of BaO·6Fe$_2$O$_3$. The contents of BaO·4.5Fe$_2$O$_3$ and BaO·6Fe$_2$O$_3$ in the products obtained by autoclaving β-FeO(OH) suspensions at 200 and 300 °C were much smaller than those in the products from γ-FeO(OH) suspensions at corresponding temperatures. When α-Fe$_2$O$_3$ was used as the starting material, autoclaving gave rise to the growth of fine particles in needle-like particles. A very small amount of hexagonal plate-like particles of BaO·2Fe$_2$O$_3$ besides α-Fe$_2$O$_3$ was, however, found in the product obtained by autoclaving at 300 °C.

Similar experiments were carried out using powders



(a) (b) (c)

Fig. 2. Electronmicrographs of α-FeO(OH)(a), β-FeO(OH)(b), and γ-FeO(OH)(c) powders (Table 1).

Table 1. Products obtained by autoclaving of suspensions containing 0.18M-$Ba(OH)_2$

Starting material	S(m^2/g)	Autoclaving temperature			
		150 °C	200 °C	250 °C	300 °C
α-FeO(OH)	23.2	α-FeO(OH)	α-FeO(OH)+B	α-Fe_2O_3+B	B
β-FeO(OH)	26.0	—	α-FeO(OH) +α-Fe_2O_3+A	α-Fe_2O_3	α-Fe_2O_3+B
γ-FeO(OH)	21.1	α-FeO(OH)+A	α-Fe_2O_3+A	α-Fe_2O_3+B	α-Fe_2O_3+B
α-Fe_2O_3[a)]	110.5	—	—	α-Fe_2O_3	α-Fe_2O_3+C

A=BaO·4.5Fe_2O_3, B=BaO·6Fe_2O_3, C=BaO·2Fe_2O_3.

a) Obtained from α-FeO(OH) with 23.2 m^2/g.

of α- and γ-FeO(OH) with different mean particle sizes. The results indicate that the decrease in the apparent density (g/ml) of iron(III) hydroxide oxide in the starting suspension was favorable for the formation of BaO·6Fe_2O_3. The apparent density decreased with a decrease in the mean particle size down to a size corresponding to about 20 m^2/g in S. When the size was too small (S>40 m^2/g), the apparent density increased as a result of the aggregation of very fine needle-like particles caused by drying during the course of the preparation of iron(III) hydroxide oxides.

In order to study the effect of the $Ba(OH)_2$ concentration on the formation of BaO·6Fe_2O_3, alkaline suspensions containing α-FeO(OH) particles (Table 1) and different amounts of $Ba(OH)_2$ (0.32—72 mmol, corresponding to 0.015—2.88 M $Ba(OH)_2$), were subjected to autoclaving at 300, 250, and 200 °C. The contents of BaO·6Fe_2O_3 in the products were determined by comparing the relative intensities of X-ray diffraction peaks of d(006) 3.86 Å for BaO·6Fe_2O_3, and d(104) 2.69 Å for α-Fe_2O_3, and d(103) 3.19 Å for BaO·2Fe_2O_3. The contents are plotted against the $Ba(OH)_2$ concentration at three reaction temperatures (Fig. 3). The content of BaO·6Fe_2O_3 in the products consisting of BaO·6Fe_2O_3 and α-Fe_2O_3 increases with an increase in the $Ba(OH)_2$ concentration and reaches 100% with 0.18—0.24 M $Ba(OH)_2$ for autoclaving at 300 °C, 0.24—0.28 M at 250 °C, and 0.36 M or more at 200 °C. A further increase in $Ba(OH)_2$ concentration at 300 and 250 °C resulted in the formation of BaO·2Fe_2O_3 besides BaO·6Fe_2O_3 and the content of BaO·2Fe_2O_3 reached 100% with 1.44 M $Ba(OH)_2$. At 200 °C, a further increase in $Ba(OH)_2$ concentration caused no formation of BaO·2Fe_2O_3, but only hindered the growth of BaO·6Fe_2O_3 particles.

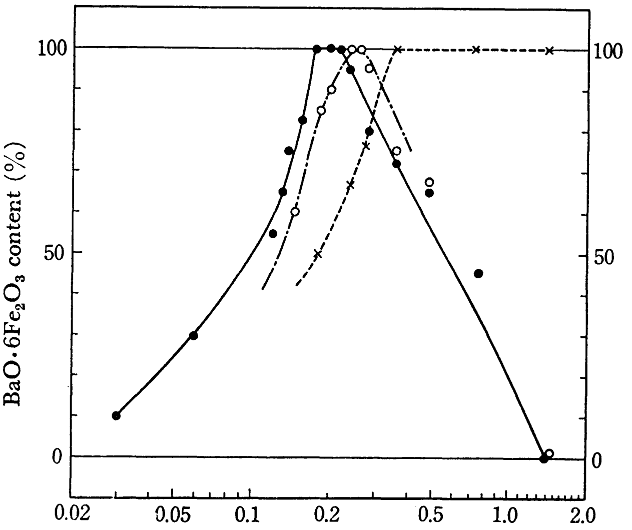


Fig. 3. Effect of $Ba(OH)_2$ concentration on BaO·6Fe_2O_3 formation at 200(×), 250(○), and 300 °C(●).

In order to examine the effect of reaction time on the content of BaO·6Fe_2O_3 in the product, the suspensions containing α-FeO(OH) (Table 1) and 0.14, 0.18, and 0.29 M $Ba(OH)_2$ were subjected to autoclaving at 250 and 300 °C for 5 min, 1/2, 2, and 8 h. In all cases, except for the reaction at 250 °C with 0.14 M $Ba(OH)_2$, α-FeO(OH) was completely transformed into BaO·6Fe_2O_3 or a mixture of BaO·6Fe_2O_3 and BaO·2Fe_2O_3 or α-Fe_2O_3 in 5 min. Under the conditions of 250 °C and 0.14 M $Ba(OH)_2$, BaO·6Fe_2O_3 was hardly formed in 5 min; however, α-FeO(OH) was completely transformed into a mixture of BaO·6Fe_2O_3 and a small amount of α-Fe_2O_3 in 2 h. The contents of BaO·6Fe_2O_3 in the products at complete transformation were not determined by the reaction time, but by the concentration of $Ba(OH)_2$ and the temperature, as is shown in Fig. 3.

γ-FeO(OH) as well as iron(III) hydroxide is unstable

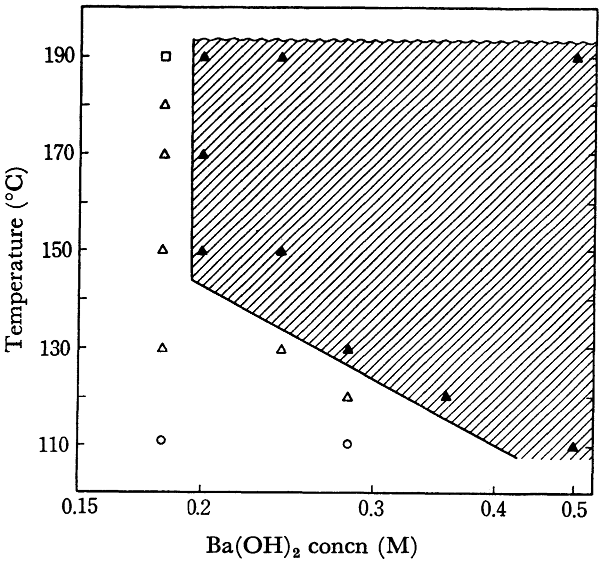


Fig. 4. The transformation products of γ-FeOOH in suspension media with various amounts of $Ba(OH)_2$. ▲ BaO·4.5Fe_2O_3, △ BaO·4.5Fe_2O_3+α-FeO(OH), ○ BaO·4.5Fe_2O_3+γ-FeO(OH), □ BaO·4.5Fe_2O_3+α-Fe_2O_3+α-FeO(OH).

in an alkaline medium and is transformed into α-FeO(OH) at temperatures lower than those needed for the transformation into α-Fe_2O_3.[12,13] The precipitate of $BaO \cdot 4.5Fe_2O_3$ seems to be formed in the presence of $Ba(OH)_2$ at temperatures at which γ-FeO(OH) is transformed into α-FeO(OH) (Table 1). In order to confirm this assumption, the following experiments were carried out using γ-FeO(OH) (Table 1). Alkaline γ-FeO(OH) suspensions containing different amounts of $Ba(OH)_2$ were subjected to autoclaving at temperatures in the range of 110—190 °C. The products are shown in Fig. 4 in relation to the temperature and the $Ba(OH)_2$ concentration (in M). Products consisting only of $BaO \cdot 4.5Fe_2O_3$ can be obtained by choosing the $Ba(OH)_2$ concentration and temperature.

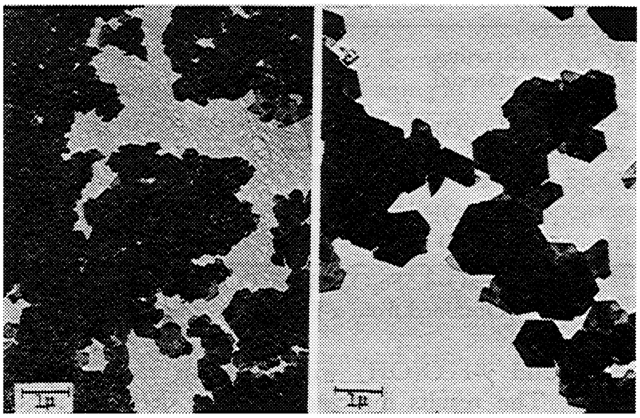
In order to examine if $BaO \cdot 6Fe_2O_3$ is formed by the dissolution of the barium ion in the particles of $BaO \cdot 2Fe_2O_3$ or $BaO \cdot 4.5Fe_2O_3$ into a solution, two suspensions of $BaO \cdot 2Fe_2O_3$ (2 g) and $BaO \cdot 4.5Fe_2O_3$ (2 g) in water (25 ml) were subjected to autoclaving at 300 °C for 5 h. Some particles of $BaO \cdot 2Fe_2O_3$ were transformed into α-Fe_2O_3, while $BaO \cdot 4.5Fe_2O_3$ was completely transformed into a mixture of $BaO \cdot 6Fe_2O_3$ and α-Fe_2O_3. When 0.14 M-$Ba(OH)_2$ containing $BaO \cdot 4.5Fe_2O_3$ was used, the product consisted of only $BaO \cdot 6Fe_2O_3$. It may be considered from the experimental results that some or all of the $BaO \cdot 6Fe_2O_3$ particles in the products obtained from β- and γ-FeO(OH) suspensions are formed *via* $BaO \cdot 4.5Fe_2O_3$.

The transformation processes could be summarized as follows:

$$\begin{tikzcd}
\alpha\text{-}Fe_2O_3 \arrow[r] & BaO \cdot 2Fe_2O_3 \\
\alpha\text{-}FeO(OH) \arrow[u] \arrow[r] \arrow[ur] & BaO \cdot 6Fe_2O_3 \arrow[u] \\
\begin{array}{l}\gamma\text{-}FeO(OH) \\ Fe(OH)_3\end{array} \arrow[u] \arrow[r] \arrow[ur] & BaO \cdot 4.5Fe_2O_3 \arrow[u]
\end{tikzcd}$$

No direct transformations, such as α-$Fe_2O_3 \rightarrow BaO \cdot 6Fe_2O_3$ and α-FeO(OH)→$BaO \cdot 4.5Fe_2O_3$, take place. Since β-FeO(OH) did not favor the formation of $BaO \cdot 6Fe_2O_3$, its yield being very small as compared with those of α-FeO(OH) and γ-FeO(OH), experiments using β-FeO(OH) were not sufficiently carried out.

The change in the shape and size of the particles before and after the transformation was observed in electronmicrographs. The change in particle shape and size suggests that the mechanism of formation takes place in the suspension medium. The barium ions in the alkaline suspension medium might react either with iron(III) ions on the surface of the particle of the intermediate product (the precursor of each product) or with iron(III) complexes formed by the dissolution of the intermediate product particle in the suspension medium to form a nucleus of $BaO \cdot 6Fe_2O_3$, $BaO \cdot 4.5Fe_2O_3$, or $BaO \cdot 2Fe_2O_3$. It is probable that the product formation takes place by the dissolution, followed by crystallization on suitable nuclei.



(a) (b)

Fig. 5. Electronmicrographs of $BaO \cdot 6Fe_2O_3$ precipitates obtained by autoclaving of iron(III) hydroxide (a) and α-FeO(OH) (b) suspensions at 300 °C.

Properties of Precipitates. The ferromagnetic products, $BaO \cdot 6Fe_2O_3$, with a hexagonal crystal structure (a=5.88 and c=23.2 Å),[14] consisted o hexagonal plate-like particles. Their size increased with a rise in the reaction temperature; it depended also on the size of the particles in the starting suspension (Fig. 5). The diameter and thickness of the hexagonal plate-like particles obtained from the suspensions of iron(III) hydroxide did not exceed 1 and 0.05 μm respectively. The diameter of the particles obtained from the suspensions of α-FeO(OH) was 1—2 μm, the thickness depending on the conditions under which they were formed. These products** contained greater amounts of barium ions than those calculated from the $BaO \cdot 6Fe_2O_3$ formula. The relative heights of the X-ray diffraction peaks vary with the sample (Figs. 6(a)—(c)). This is because the hexagonal plate-like particles in the pressed powdery sample for X-ray measurement undergo alignment to some extent. The degree of alignment, F, depends on the thickness, d, of the particles (1—2 μm in diameter) and on the packing density P (Table 2). The d values were calculat-

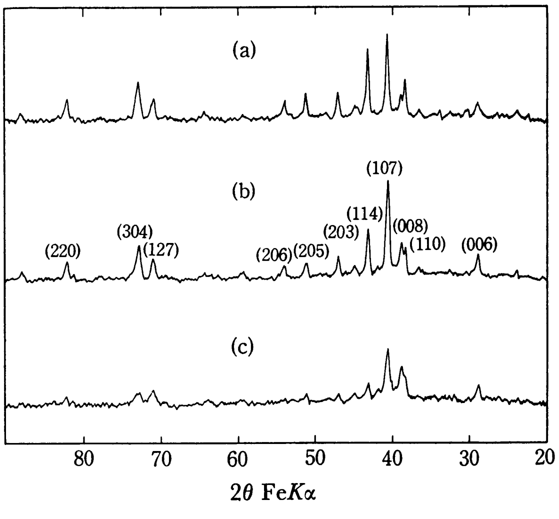


Fig. 6. X-Ray diffraction patterns of $BaO \cdot 6Fe_2O_3$ precipitates 1—2 μm in dia. and 0.17 (a), 0.08 (b), and 0.03 μm (c) in d.

** Contained less than 0.4 wt% of Fe^{2+}

Table 2. Alignment degree F and packing density P of compacts prepared by pressing $BaO \cdot 6Fe_2O_3$ powders with particle dia. 1—2 μm at pressures

S (m²/g)	d (μm)	10 kg/cm² F	10 kg/cm² P	100 kg/cm² F	100 kg/cm² P	1000 kg/cm² F	1000 kg/cm² P
9.65	0.041	0.09	0.98	0.26	1.64	0.37	2.67
6.75	0.060	0.23	1.09	0.48	2.06	0.56	2.72
5.25	0.079	0.26	1.27	0.36	1.90	0.49	2.72
2.69	0.168	0.09	1.50	0.21	2.20	0.35	2.78

$F = I_{d(008)}/I_{d(008)} + I_{d(107)}$, where $I_{d(008)}$ and $I_{d(107)}$ are relative intensities of X-ray diffraction on (008) and (107) crystal faces, respectively, of $BaO \cdot 6Fe_2O_3$.

ed by means of this formula;

$$d(\mu m) = 3(3)^{1/2}/1.5\rho S(3)^{1/2} - 6$$

assuming that the diameter of the circle circumscribing the hexagon is 2 μm, where $\rho = 6.3$ is the specific gravity of the $BaO \cdot 6Fe_2O_3$ crystal.

Since the c axis of the $BaO \cdot 6Fe_2O_3$ crystal is the easy direction of magnetization, all the hexagonal plate-like particles can be aligned by magnetic field when they are free to rotate. A brown suspension prepared by mixing the $BaO \cdot 6Fe_2O_3$ precipitates with an adequate amount of a liquid such as oil, water, or ethanol in a test tube, loses its color when brought near a magnet since light is reflected by the aligned basal planes perpendicular to the direction of the magnetic field.

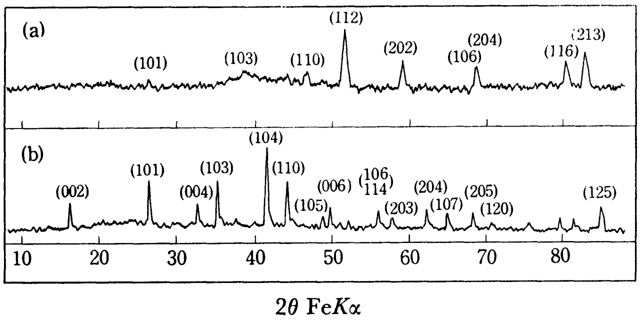


Fig. 7. X-Ray diffraction patterns of $BaO \cdot 4.5Fe_2O_3$ (a) and $BaO \cdot 2Fe_2O_3$ (b).

X-Ray diffraction patterns of the non-ferromagnetic products consisting of only one phase are shown in Figs. 7(a) and (b). Samples (a) and (b) contained barium and iron(III) ions in the Fe_2O_3/BaO mol ratios of 4.4—4.6 and 1.9—2.2 respectively. $BaO \cdot 4.5Fe_2O_3$ is estimated to have a hexagonal crystal structure with $a = 4.8$ and $c = 11.3$ Å. The particles were spherical (maximum size, 0.05 μm). It was difficult to obtain large particles. Particles of $BaO \cdot 2Fe_2O_3$ remarkably increase in size with increases in the temperature and in the concentration of $Ba(OH)_2$. Large particles with a hexagonal crystal structure with $a = 5.12$ and $c = 13.8$ Å were easily obtained by autoclaving at 300 °C. Their properties were then studied.[3,15]

When heated at 800 °C in the air for 4 h, the $BaO \cdot 4.5Fe_2O_3$ particles were decomposed into $BaO \cdot 6Fe_2O_3$ and a small amount of $BaO \cdot Fe_2O_3$, whereas the $BaO \cdot 2Fe_2O_3$ particles, 20—40 μm in diameter, were hardly decomposed at all. This difference might be due to the difference in their particle size.

Magnetic Properties of $BaO \cdot 6Fe_2O_3$ Precipitates. The products were obtained from α-FeO(OH) suspensions containing various amounts of $Ba(OH)_2$ at 200, 250 and 300 °C under the conditions shown in Fig. 3. The samples, consisting of hexagonal plate-like particles 1—2 μm in diameter, were selected, pressed in brass cylinders 15 mm in diameter and 5 mm in height, and sandwiched between the pole pieces of a magnet. After the sample had been magnetized at $\boldsymbol{H} = 17$ kOe, the demagnetization curve was obtained from 5 kOe with a self-recording permeameter. The results are given in Table 3. As the d value increases to 0.044 μm, the values of $4\pi I/P$ and ${}_i\boldsymbol{H}_c$ increase. The d dependence of $4\pi I/P$ and ${}_i\boldsymbol{H}_c$ might indicate the presence of superparamagnetic particles in the samples with $d \leqq 0.044$ μm.

Table 3. Magnetic properties of $BaO \cdot 6Fe_2O_3$ precipitates

Preparation conditions: Autoclaving temp.	Preparation conditions: Concn $Ba(OH)_2$ (M)	S (m²/g)	d (μm)	P (g/ml)	$4\pi I/P$ (G)	${}_iH_c$ (Oe)	I_r/I
200 °C	0.72	20.8	0.016	0.92	210	286	0.41
	0.48	17.5	0.019	1.12	120	606	0.62
	0.36	8.1	0.041	0.86	230	813	0.57
250 °C	0.28	7.6	0.044	1.11	520	973	0.72
	0.24	6.7	0.050	0.95	480	942	0.59
	0.20	6.6	0.051	1.29	480	942	0.63
300 °C	0.20	5.2	0.066	0.93	510	1042	0.55
	0.18	4.1	0.085	0.92	490	1003	0.65

Samples 1—2 μm in diameter and 0.15 μm or less in d were prepared under various conditions. The saturation magnetization, σ_s, at 17 kOe and the ${}_i\boldsymbol{H}_c$ were also measured in the P range of 0.9—2.2 g/ml at room temperature. The values of the samples with $0.05 \leqq d \leqq 0.15$ μm were 55 ± 4 in σ_s (emu/g) and 0.9—1.0 kOe in ${}_i\boldsymbol{H}_c$. The samples were calcined in the air at ≈1000 °C. It was found that no remarkable difference in σ_s and ${}_i\boldsymbol{H}_c$ occurred between the calcined and the original samples.

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