

The Formation of $\text{SrFe}_{12}\text{O}_{19}$ from Aqueous Suspensions and Its Properties

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Alkaline suspensions, containing iron(III) hydroxide, Sr(II) and excess NaOH, were subjected to autoclaving at temperatures between 150 and 300°C, and the properties of the resulting products were studied. A ferromagnetic precipitate, consisting of hexagonal, platelike particles with 2 μm or less in diameter was obtained by a suitable combination of the temperature and the concentrations of Fe(III), Sr(II) and excess NaOH. A nonferromagnetic precipitate was formed in place of $\text{SrFe}_{12}\text{O}_{19}$ at temperatures lower than those for the formation of $\text{SrFe}_{12}\text{O}_{19}$. The formation of $\text{SrFe}_{12}\text{O}_{19}$ was hindered in the presence of a slight amount of carbonates, but facilitated in the presence of sulfates. The magnetic properties of the $\text{SrFe}_{12}\text{O}_{19}$ samples were investigated at room temperature.

KEY WORDS: $\text{SrFe}_{12}\text{O}_{19}$ / Hexagonal-platelike particles/ Ferromagnetic precipitate/ Coercivity/ Autoclaving/ Alkaline suspension/

Strontium ferrite, $\text{SrFe}_{12}\text{O}_{19}$, being one of the M-type hexagonal ferrites, is widely used as economical permanent magnets, and its properties have been well investigated.¹⁾ In general this ferromagnetic material can be obtained as a polycrystalline substance when a mixture of iron(III) oxide and strontium carbonate is ignited at high temperatures (above 1100°C) in an oxidizing gas.

The hydrothermal synthesis of $\text{SrFe}_{12}\text{O}_{19}$ was achieved for the first time in 1983 by two (M. K. and T. T.) of the present authors.²⁾ Some conditions for the formation of $\text{SrFe}_{12}\text{O}_{19}$ by autoclaving were investigated by Lee et al.³⁾ and by Hamamura et al.⁴⁾ In the present study, it was found that iron(III) hydroxide can react only in the absence of carbonates with strontium ions, Sr(II), in an alkaline suspension to form $\text{SrFe}_{12}\text{O}_{19}$ if we choose the appropriate concentrations of Fe(III), Sr(II), and excess NaOH, and a suitable reaction temperature in the autoclaving preparation. The presence of a slight amount of carbonates in the starting, alkaline suspension containing Fe(III) and Sr(II) hindered the formation of $\text{SrFe}_{12}\text{O}_{19}$. Although it was difficult to always obtain the starting suspensions containing no carbonates, it has been found that the presence of sulfates in the starting suspensions containing slight amounts of carbonates facilitates the formation of $\text{SrFe}_{12}\text{O}_{19}$. A nonferroma-

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gnetic compound with the crystal structure similar to that of $\text{BaO}\cdot 4.5\text{Fe}_2\text{O}_3$ is also obtained at temperatures lower than those at which $\text{SrFe}_{12}\text{O}_{19}$ is formed.

This paper describes the conditions in the absence or presence of sulfates for the formation of $\text{SrFe}_{12}\text{O}_{19}$ and its magnetic properties at room temperature.

EXPERIMENTAL

An acidic solution was prepared in the 1 dm³ autoclave made of stainless steel, by mixing aqueous solutions of strontium nitrate, sodium sulfate, and either iron(III) chloride or nitrate (each of reagent grade). To this an excess of an NaOH solution was added in a required amount and diluted with conductivity water to 0.7 dm³. A number of alkaline suspensions, each containing 0.9 M ($M = \text{mol/dm}^3$) Fe(III), were prepared by varying the concentrations of excess NaOH, Sr(II), and SO_4^{2-} in the ranges, respectively, from 0.1 to 6.0 M, 0.08 to 0.9 M, and 0 to 1.0 M. They were heated to the desired temperatures at a rate of 4°C/min and kept at 150, 200, 250, and 300°C with mechanical stirring at 750 rpm for a fixed time of 5h and then allowed to cool to room temperature. The resulting products were separated by filtration, treated with 1 M HCl to remove remaining Sr(II) as carbonate, well washed with water, and then dried at 80°C in air.

The products were subjected to examinations with X-ray diffraction using Fe $K\alpha$ radiation (XRD), transmission and scanning electron microscopic observation (TEM and SEM), and to the BET surface area measurement using nitrogen. Magnetic measurements on the ferromagnetic samples packed with $1.2 \pm 0.5 \text{ g/cm}^3$ in a brass cylinder of 0.6 cm in diameter and 0.2 cm in height, were carried out at room temperature in a magnetic field up to 10 kOe ($1 \text{ kOe} = 10^6/4\pi \text{ Am}^{-1}$), using a vibrating-sample magnetometer.

RESULTS AND DISCUSSION

The starting, alkaline suspensions containing no sulfates were prepared by using iron(III) chloride as an iron salt and subjected to autoclaving at temperatures between 150 and 300°C. Ferromagnetic, brownish precipitates, consisting of $\text{SrFe}_{12}\text{O}_{19}$ with or without $\alpha\text{-Fe}_2\text{O}_3$, were formed at 200°C or above, depending on the concentrations of excess NaOH and Sr(II). On the other hand, at 150°C, nonferromagnetic precipitates in place of $\text{SrFe}_{12}\text{O}_{19}$, consisting of extremely fine particles with the similar crystal structure to that of $\text{BaO}\cdot 4.5\text{Fe}_2\text{O}_3$ were formed.⁵⁾ The properties of typical $\text{SrFe}_{12}\text{O}_{19}$ samples are given in Table 1. The nonferromagnetic precipitates were formed with $\alpha\text{-Fe}_2\text{O}_3$ at 200°C in the presence of 0.22 M Sr(II) with excess NaOH of the concentration lower than 0.6 M. The values of BET surface area, S , of the resulting $\text{SrFe}_{12}\text{O}_{19}$ samples became greater with an increase to 0.9 M in the Sr(II) concentration, and with decreases both in the excess NaOH concentration and the temperature. The values of magnetization, M ($1 \text{ emu/g} = 4\pi\rho 10^{-4} \text{ T}$, where $\rho = 5.0$ is specific gravity), at 10 kOe and coercive force, H_c , depended on the conditions for their formation.

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Table 1. Properties of the Typical $\text{SrFe}_{12}\text{O}_{19}$ Samples Prepared by Autoclaving at Different Temperatures, T, of Aqueous Suspensions Containing 0.9M Fe(III), and Different Concentrations of Sr(II) and of Excess NaOH.

Sample	Sr(II) /M	Excess NaOH/M	T/ $^{\circ}$ C	S/m ² g ⁻¹	M/emu g ⁻¹	Hc/kOe
A	0.90	0.6	200	82	23	0.6
B	0.22	0.6	200	27	41	1.4
C	0.22	6.0	200	9	39	0.9
D	0.90	0.6	300	40	36	1.3
E	0.45	0.6	300	8	48	1.4
F	0.22	6.0	300	8	47	1.0
G	0.22	0.1	300	8	48	1.0

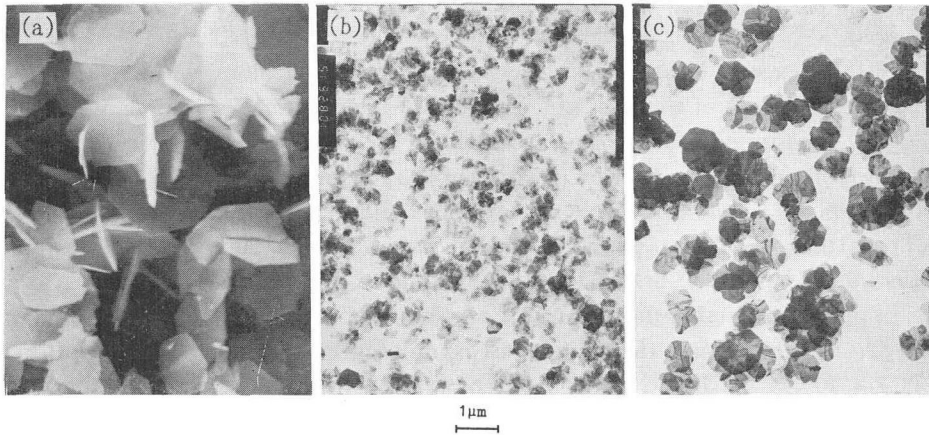


Fig. 1. Electron-micrographs of $\text{SrFe}_{12}\text{O}_{19}$ samples C(a, with SEM), D (b, with TEM) and E (c, TEM).

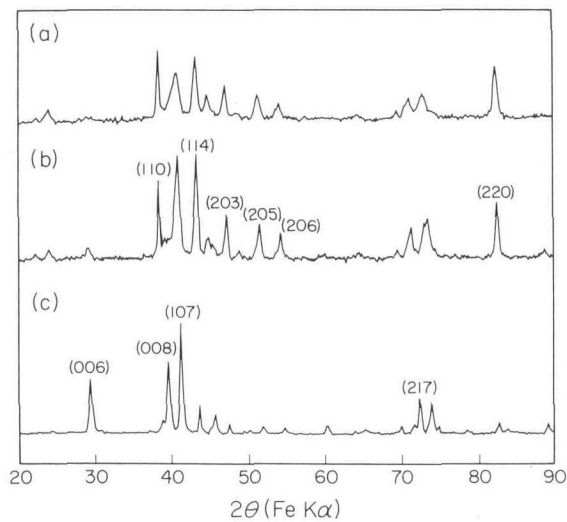


Fig. 2. XRD patterns of $\text{SrFe}_{12}\text{O}_{19}$ samples A(a), D(b), and G(c).

The $\text{SrFe}_{12}\text{O}_{19}$ samples were found by SEM and TEM graphs to consist of hexagonal, platelike particles whose diameter was 2 μm or less, depending strongly on the concentration of Sr(II) (Fig. 1). The relative heights of the XRD peaks vary with the sample (Fig. 2). This was because the particles in the pressed powdery sample for the XRD examination underwent alignment to some extent. The degree of alignment depended on the thickness and the cross-sectional shape of the particles and on the packing density.

When similar experiments were carried out with iron(III) nitrate in place of the chloride, no marked differences were found both in the conditions for the $\text{SrFe}_{12}\text{O}_{19}$ formation and in the properties of the resulting products. A decrease to 0.3 M in the Fe(III) concentration in the starting suspensions under the conditions where $\text{SrFe}_{12}\text{O}_{19}$ was formed caused no remarkable differences in the magnetic properties and in the particle shape and size of the products, irrespective of the kind of the iron salts used.

In these experiments, $\alpha\text{-Fe}_2\text{O}_3$ was sometimes formed along with $\text{SrFe}_{12}\text{O}_{19}$, regardless of the kind of the iron salt used under the identical conditions where only $\text{SrFe}_{12}\text{O}_{19}$ was formed. The $\alpha\text{-Fe}_2\text{O}_3$ content in the products was governed by slight differences in the conditions of preparation of the starting suspensions even in a nitrogen atmosphere. It is considered that part of the Sr(II) precipitated as a carbonate in the starting, alkaline suspension and that the presence of such a stable precipitate hinders the formation of $\text{SrFe}_{12}\text{O}_{19}$ in the alkaline suspension.

In order to examine the effect of the presence of carbonates on the formation of $\text{SrFe}_{12}\text{O}_{19}$ by autoclaving, the suspensions containing 2 or 6M excess NaOH, 0.15 M $\text{Sr}(\text{NO}_3)_2$, 0.9 M FeCl_3 and either 0.075 or 0.18 M Na_2CO_3 , were prepared by mixing the acidic solution and alkaline solutions containing both NaOH and Na_2CO_3 , and then subjected to autoclaving at 200 and 300°C. The sample prepared in the presence of 0.075 M Na_2CO_3 and 6 M excess NaOH at 300°C consisted of $\text{SrFe}_{12}\text{O}_{19}$ with $\alpha\text{-Fe}_2\text{O}_3$, but under the other conditions, only $\alpha\text{-Fe}_2\text{O}_3$ was obtained, as far as our experiments were concerned.

It has been known that SrSO_4 is stable in an acidic medium, but unstable in an alkaline one as compared with SrCO_3 . In fact, when the suspensions containing 6 M excess NaOH, 0.15 M $\text{Sr}(\text{NO}_3)_2$, 0.9 M $\text{Fe}(\text{NO}_3)_3$, 0.075 or 0.18 M Na_2CO_3 and 0.18 or 0.5 M Na_2SO_4 were prepared by mixing the acidic solutions containing sulfates and the alkaline solutions containing carbonates, and then subjected to autoclaving at 300°C, the $\alpha\text{-Fe}_2\text{O}_3$ content in the products was shown by XRD to decrease with increasing sulfate/carbonate mol ratio. Similar experiments were carried out by using FeCl_3 in place of the nitrate. The use of FeCl_3 somewhat facilitated the formation of $\text{SrFe}_{12}\text{O}_{19}$ by autoclaving. Consequently, the presence of a slight amount of carbonates with sulfates is not presumed to hinder the formation of $\text{SrFe}_{12}\text{O}_{19}$.

In order to examine the effect of the presence of sulfates on the formation of $\text{SrFe}_{12}\text{O}_{19}$, experiments were also conducted by using the acidic solutions containing $\text{Fe}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$ and Na_2SO_4 , in which the formation of a whitish precipitate (SrSO_4) was hardly observed. The starting suspensions with 1.2 in the mol ratio of $\text{SO}_4^{2-}/\text{Sr}(\text{II})$ with various concentrations of excess NaOH, Sr(II) and SO_4^{2-} were

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 Table 2. Properties of the SrFe₁₂O₁₉ Samples Prepared in the Presence of Sulfates

Sample	Sr(NO ₃) ₂ /M	Na ₂ SO ₄ /M	Excess NaOH/M	T/°C	S /m ² g ⁻¹	M /emu g ⁻¹	Hc /kOe
H	0.22	0.27	6	200	13	46	1.1
I	0.15	0.18	6	200	16	47	1.2
J	0.15	0.18	2	200	24	48	1.6
K	0.15	0.18	6	250	11	50	1.0
L	0.15	0.18	6	300	9	50	1.0
M	0.15	0.18	2	300	10	54	0.8
N*	0.10	0.12	6	300	5	42	0.8

*Consisting of a slight amount of α -Fe₂O₃.

subjected to autoclaving at temperatures between 150 and 300°C. Extensive experiments on the effect of temperature by using the suspensions containing sulfates demonstrated that the products consisted of either the hexagonal platelike SrFe₁₂O₁₉ particles with 2 μ m or less in diameter at above 200°C, or the nonferromagnetic particles at 150°C, with or without SrSO₄ and α -Fe₂O₃. It was also shown that the SrSO₄ content in the products decreased with increasing the concentration of excess NaOH as will be described below. The properties of some typical SrFe₁₂O₁₉ samples are given in Table 2. In addition to these results, when the concentrations of excess NaOH were 1.5 M at 0.15 M Sr(II) and 2.0 M at 0.22 M Sr(II), the samples prepared at 200°C were found by XRD to consist of SrSO₄ besides SrFe₁₂O₁₉ and slight amounts of α -Fe₂O₃, the contents of SrSO₄ and α -Fe₂O₃ increasing with a decrease in the concentration of excess NaOH.

In order to examine the effect of the concentration of sulfates on the formation of SrFe₁₂O₁₉, the suspensions containing 6 M excess NaOH, 0.08 M Sr(II), and 0.9 M Fe(NO₃)₃ with varying the concentration of sulfates from 0.1 to 1.0 M, were subjected to autoclaving at 300°C. The M values increased from 19 to 33 emu/g with increasing the concentration of sulfates to 1 M as a result of a decrease in the α -Fe₂O₃ content in the products. This result suggests that the amount of excess Sr(II) required for the formation of SrFe₁₂O₁₉ in the strongly alkaline suspension becomes smaller with an increase in the concentration of sulfates.

The effect of the reaction time on the properties of the SrFe₁₂O₁₉ precipitates was examined as follows. The suspensions were subjected to autoclaving by varying the time as 2, 10 and 20 h under the conditions where the samples A, D, F (Table 1), and J (Table 2) had been prepared. The M, Hc and S values of the products obtained in the absence of sulfates after 5 h at 200°C and 2 h at 300°C under the identical conditions for each reaction process were almost independent of the reaction time.

On the other hand, the M and S values of the SrFe₁₂O₁₉ samples prepared in the presence of sulfates gradually changed, respectively, from 45 to 53 emu g⁻¹ and from 37 to 14 m²g⁻¹ with the time without a change in Hc. In this case, the XRD peaks for the (00l) planes of the SrFe₁₂O₁₉ samples became relatively higher and somewhat sharper with the time.

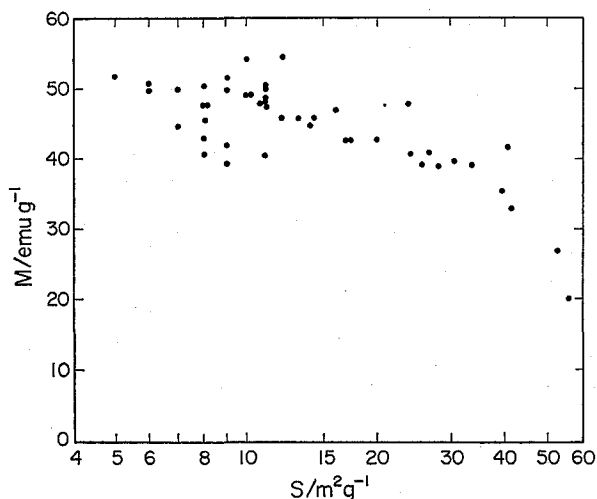


Fig. 3. Magnetization, M , at 10 kOe of $\text{SrFe}_{12}\text{O}_{19}$ samples plotted against their S values.

The M values of the $\text{SrFe}_{12}\text{O}_{19}$ samples with $5 \leq S \leq 60 \text{ m}^2/\text{g}$ prepared in the presence or absence of sulfates under various conditions are plotted against the S values in Fig. 3. Presumably, an increase in the S causes an increase in the fraction of nonferromagnetic portion, which is reported to be the subsurface of the ferromagnetic particle, such as $\gamma\text{-Fe}_2\text{O}_3$, NiFe_2O_4 , CrO_2 ,⁶⁾ or $\text{BaFe}_{12}\text{O}_{19}$ particle.⁷⁾ In the range $5 \leq S \leq 20 \text{ m}^2/\text{g}$, the M values depend slightly on the S values, being between 40 and 55 emu/g at $S \approx 10 \text{ m}^2/\text{g}$. The difference in the M values among the samples with the same S values seems to be due to the difference in the distributions of the particle shapes with three dimensional forms. Namely, since the $[00l]$ direction of the $\text{SrFe}_{12}\text{O}_{19}$ crystal is the easy direction of magnetization, the difference in the M values is considered to depend on the fraction of the $(00l)$ surface area. The H_c values of the samples were between 0.7 and 1.6 kOe. The H_c values of these samples are lower than those of the ones prepared by a solid state reaction. Such low H_c values below 2 kOe might have resulted from the large sectional-shape anisotropy of each particle.

REFERENCES

- (1) H. Kojima, "Ferromagnetic Materials", Vol. 3 Ed. by E.P. Wohlfarth, North-Holland Publishing Company, Amsterdam (1982) pp. 307-366.
- (2) M. Kiyama and T. Takada, Jpn. Kokai Tokkyo Koho, 58-110432 (1983).
- (3) K.-H. Lee, B.-H. Lee, and S.-K. Kim, *J. Korean Ceram. Soc.*, **24**, 17 (1987).
- (4) A. Hamamura, T. Miyashima and F. Kikui, Jpn. Kokai Tokkyo Koho, 63-64307 (1988).
- (5) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **49**, 1855 (1976).
- (6) A.H. Morrish and K. Haneda, *J. Magn. Magn. Mater.*, **35**, 105 (1983).
- (7) H. Yamada, T. Takano, M. Kiyama, T. Takada, T. Shinjo, and K. Watanabe, *Advances in Ceramics*, Vol. 16, 4th Intern. Conf. Ferrites, Am. Ceram. Soc., (1986) p. 169.