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The Formation of β-$LiFe_5O_8$ from Aqueous Suspensions and Its Properties

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Alkaline suspensions containing iron(III) hydroxide and excess LiOH were subjected to aging at temperatures between 40 and 90 °C or to autoclaving at 120 °C or above. The resulting products, identified by X-ray analysis as a spinel phase, were further subjected to magnetic examination at 300 K, BET surface-area measurements, and electron-microscopic observation. The ferromagnetic precipitates of β-$LiFe_5O_8$ were formed at lower temperatures and less excess LiOH concentrations than those at which the nonferromagnetic precipitates of α-$LiFeO_2$ were formed. Their saturation magnetization increased near 60 emu g^{-1} (1 emu $g^{-1}=4\pi\rho 10^{-4}$ T, where ρ=specific gravity) with the increase in their mean particle size, D, their coercive force depending on the D. With a rise in the temperature of the suspension, superparamagnetic particles with vacancies of the Li ion, intermingled with the ferromagnetic cubic particles, slowly grew to ferromagnetic particles and the composition approached $LiFe_5O_8$.

The ferromagnetic compounds of $LiFe_5O_8$, which has a cubic inverse spinel structure at room temperature, are obtained below 1000 °C in air by the use of a ceramic method. This compound is known to have two modifications, the ordered and disordered phases. The Li and Fe(III) ions in the octahedral(B) sites are distributed in an ordered ratio of 1:3 below 735 °C, while they are randomly disordered above 755 °C.[1] The Curie temperature and saturation magnetization are not affected by the ordering.[2]

The synthesis of $LiFe_5O_8$ from an aqueous suspension was achieved for the first time in 1980,[3] in this laboratory. In the present study, it has been found that iron(III) hydroxide can react with the Li ion in an alkaline suspension to form $LiFe_5O_8$ if we choose appropriate concentrations of the iron(III) and Li ions and a suitable reaction temperature: a nonferromagnetic precipitate of α-$LiFeO_2$ with a cubic, disordered structure[4] is also obtained.

This paper will deal with the conditions needed for the formation of $LiFe_5O_8$ and its properties.

Experimental

The starting suspensions of a gelatinous precipitate of iron(III) hydroxide were prepared by adding an excess LiOH solution to an acidic solution of iron(III) nitrate (each of an analytical grade). A number of alkaline suspensions, varying in their excess LiOH concentrations, were also prepared. Each suspension was diluted with conductivity water to 1 dm^3 in a 1.3-dm^3 flask equipped with five inlet necks. The construction of the flask was similar to what has previously been described,[5] except that an electrode for a self-recording pH meter was not inserted. The individual 1-dm^3 suspensions, containing 0.2 M (1 M=1 mol dm^{-3}) Fe(III) and different excess LiOH concentrations in the 0.03—3.0 M range, were heated and kept at desired temperatures ranging from 40 to 90 °C, and nitrogen gas was bubbled into for 5 h at a constant rate of 250 dm^3 h^{-1} for effervescent aging.

A number of alkaline suspensions (0.2 dm^3), each containing 0.2 M Fe(III), were also prepared in a 0.3-dm^3 stainless steel autoclave by varying the excess LiOH concentration in the 0.03—3.0 M range. They were then heated at the rate of 4 °C min^{-1} to the desired temperature. They were kept at temperatures ranging from 120 to 280 °C with mechanical stirring at 100 rpm for 5 h and then allowed to cool to room temperature.

The resulting products were separated by filtration, washed several times with water, treated with acetone, and then dried at 30 °C in air. The products, which were found, by means of an X-ray diffraction examination using Co $K\alpha$ radiation, to consist of the spinel phase, were then subjected to BET surface-area measurements using nitrogen and to an electron-microscopic examination. Each weighing 100 mg, they were then packed in a brass cylinder 0.6 cm in diameter and 0.2 cm in height, and magnetic measurements were carried out at room temperature in a magnetic field up to 10 kOe (1 kOe=$10^6/4\pi$ A m^{-1}), using a vibrating-sample magnetometer.

The mean particle size, D, of the $LiFe_5O_8$ samples was estimated from the BET surface area, S (m^2 g^{-1}), by assuming that the sample consisted of cubic particles with a specific gravity of 5.0. The average particle size, d, for the samples with D<50 nm was further estimated from the line broadening of the X-ray diffraction peak for the (311) plane of the $LiFe_5O_8$ crystal structure.

Results and Discussion

The formation at 0.2 M Fe(III) of the products by aging or by autoclaving is shown in Fig. 1 in terms of the concentration of the excess LiOH and the reaction temperature. Dark brown, ferromagnetic precipitates with the spinel structure are formed in the presence of an excess of LiOH of at least 0.3 M by selecting an appropriate concentration and temperature. Apparently, the range of the excess LiOH concentration needed for the formation of the ferromagnetic precipitate becomes narrower with an increase in the

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temperature beyond 120 °C. Nonferromagnetic precipitates, each consisting of spherical α-$LiFeO_2$ particles, are formed in the ranges of excess LiOH concentrations and of autoclaving temperatures higher than those at which the ferromagnetic precipitates are formed.

The properties of five typical samples with the spinel structure, A through E, are given in Table 1. Electron-microscopic examination indicates that the growth of some of the extremely fine particles with the spinel structure begins at 120 °C and is promoted by a rise in the temperature (Fig. 2). The elevation of the temperature causes a significant increase in *d*, but only a slight increase in the *D* because of the extremely fine particles remaining in each sample. An increase in the difference between the *D* and *d* values for the sample shows that the particle-size distribution becomes wider. The magnetization, *M*, at 10 kOe and the coercive force, *Hc*, depend on the *d* and *D*.

The Mössbauer spectra of several $LiFe_5O_8$ samples with different *D* values, all taken at room temperature, are shown in Fig. 3. The sample with 4.7 nm in *D* consists only of superparamagnetic particles (Fig. 3(a)), and as the *D* value increases, the superparamagnetic particles coexist with the ferromagnetic

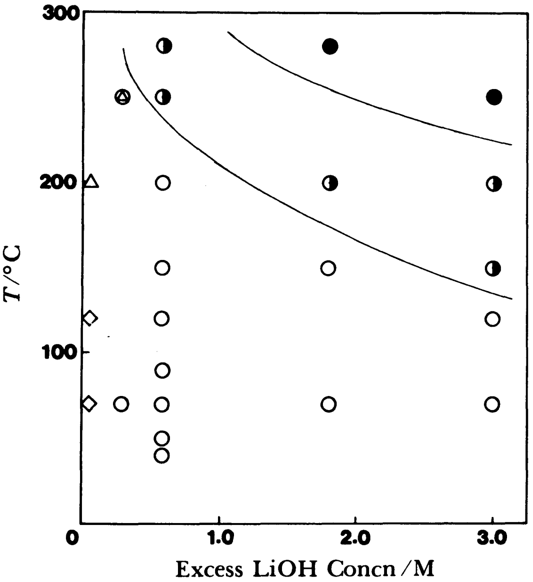

Fig. 1. Conditions for the formation at different temperatures, *T*, of $LiFe_5O_8$ from alkaline suspensions containing 0.2 M Fe(III) and various concentrations of excess LiOH.
○: $LiFe_5O_8$, ●: $LiFeO_2$, ◑: a mixture of $LiFe_5O_8$ and $LiFeO_2$, △: α-Fe_2O_3, ⊗: a mixture of α-Fe_2O_3 and $LiFe_5O_8$, ◇: α-FeO(OH).

Table 1. Typical $LiFe_5O_8$ Samples Prepared by the Aging or Autoclaving, at Various Temperatures (*T*), of Aqueous Suspensions, Each Containing 0.2 M Fe(III) and a 0.6 M Excess of LiOH

Sample	*T*/°C	*D*/nm	*d*/nm	*Hc*/Oe	*M*/emu g^{-1}
A	40	4.7	4	8	12
B	70	5.0	8	55	22
C	90	5.0	11	72	23
D	120	7.4	27	83	42
E	200	15.0	50	76	50
F[a]	250	31.0	94	75	54

a) Prepared by the use of iron(III) sulfate in place of nitrate.

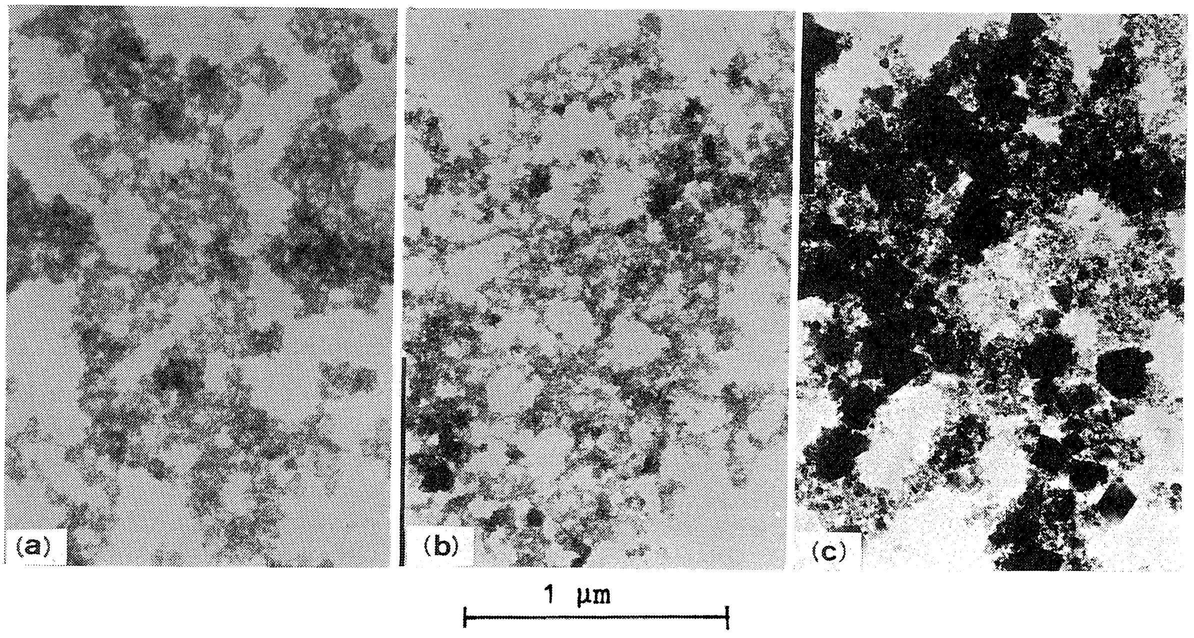

Fig. 2. Transmission electron micrographs of samples B(a), D(b), and E(c).

particles, until the former decrease (b and c). It is possible to prepare the samples with D>15 nm at 200 °C, as will be described later, by increasing the concentration of the Fe(III) in the starting suspension or by prolonging the reaction time. Such samples contained no superparamagnetic particles (Fig. 3(d)), and their hyperfine fields (49.4 T) were almost the same as that of $LiFe_5O_8$ prepared by a ceramic method.[6]

An increase in the Fe(III) concentration in the starting suspension under the conditions where the ferromagnetic precipitate was formed was found to cause an increase in D, as will be described below. The suspensions containing a 0.6 M excess of LiOH and either 0.1, 0.5, or 1.0 M Fe(III) were also prepared and subjected to autoclaving at 200 °C. The ferromagnetic precipitates thus obtained consisted of extremely fine particles, the cubic ones being 80—140 nm in size. As the Fe(III) concentration was increased, their D values increased from 14 to 23 nm without any appreciable change in the d (50—53 nm).

In order to examine the effect of the reaction time on the particle growth, suspensions, each containing 0.2 M Fe(III) and a 0.6 M excess of LiOH, were subjected to aging at 70 °C or autoclaving at 150 and 200 °C for different times (t). The t-dependence of the d and D values at 200 °C becomes significant after 10 h (Fig. 4). The extremely fine particles were found, by the use of an electron microscope, to coexist with cubic particles 100 nm in size, even in the sample prepared by autoclaving at 200 °C for 50 h.

Similar experiments were also conducted using Fe(III) chloride or sulfate in place of the nitrate. No particular difference could be found in the conditions for the formation of the ferromagnetic precipitate and for the particle growth. The temperature for the formation of the ferromagnetic precipitate in the presence of sulfates may be raised slightly, as is evidenced by Sample F in the Table.

The M values of the ferromagnetic samples prepared under various conditions are plotted against their D values in Fig. 5. The M value increases with the D, reaching near 60 emu g^{-1}. When the M values were plotted against the d, they irregularly and

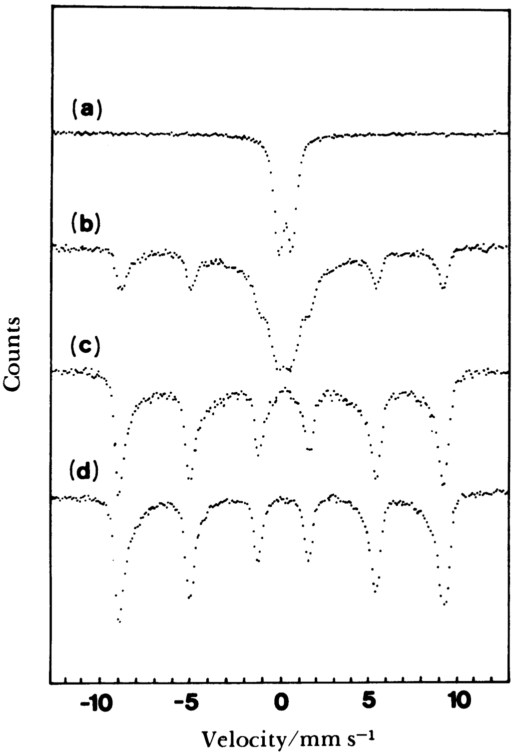

Fig. 3. Mössbauer spectra at 300 K of $LiFe_5O_8$ samples A(a), B(b), E(c), and 2E(d). Sample 2E prepared at 200 °C for 20 h (Fig. 4) and its hyperfine field is 49.4 T.

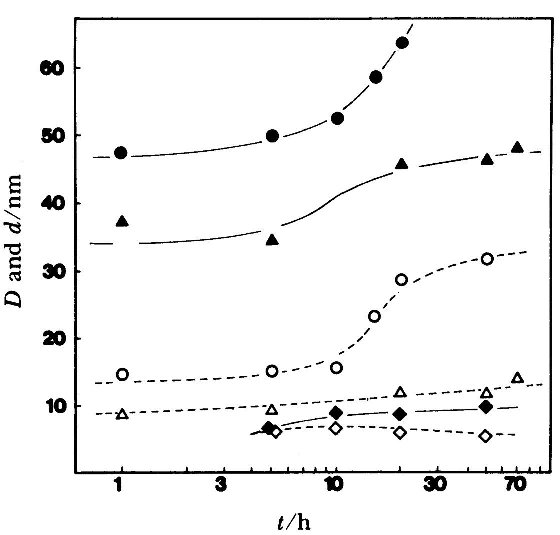

Fig. 4. Changes in the D(white) and d(black) of the samples prepared at 200 (circles), 150 (triangles), and 70 °C (tetragons) with time, t.

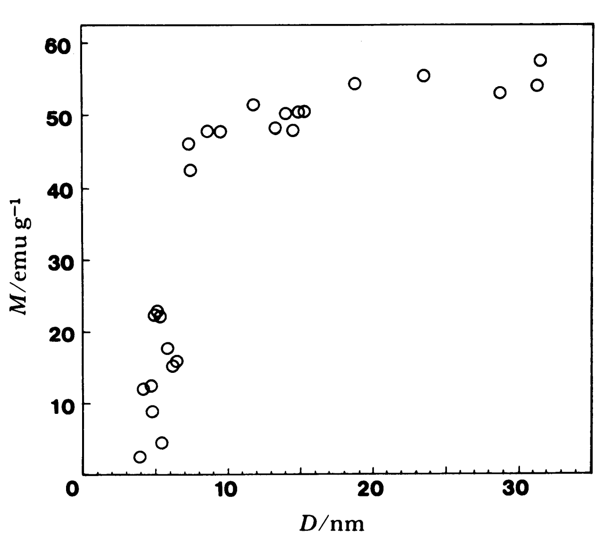

Fig. 5. Magnetization, M, at 10 kOe of $LiFe_5O_8$ samples plotted against their D values.

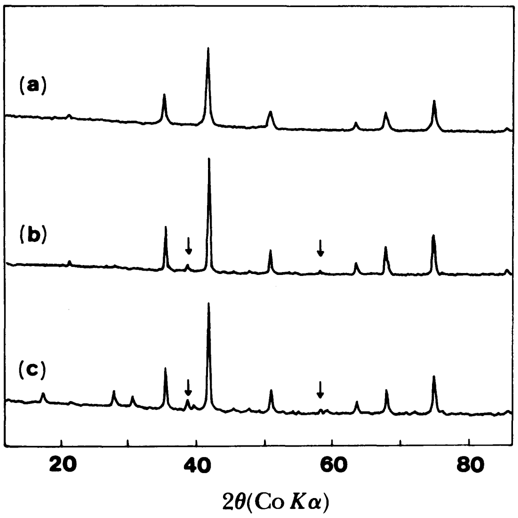

Fig. 6. X-Ray diffraction patterns of the β-$LiFe_5O_8$ sample E(a), and heat-treated samples by rapid cooling from 900 °C (b) and by slow cooling from 750 °C (c). Arrows in (b) and (c) indicate the peaks caused by the presence of α-Fe_2O_3.

remarkably increased to 40 emu g^{-1} with the increase in the d to 10 nm, while a further increase in d to 90 nm resulted in only a slight increase in M to near 60 emu g^{-1}. Presumably, an increase in the specific surface area causes an increase in the nonferromagnetic portion, which is reported to be the subsurface of the ferromagnetic particle, such as a γ-Fe_2O_3, $NiFe_2O_4$, CrO_2,[7] or $BaFe_{12}O_{19}$ particle.[8] Increasing the d values to 15 nm or the D values to 7 nm caused an increase in Hc to about 0.1 kOe as a result of the decrease in the number of superparamagnetic particles. A further increase in D or d resulted in a slight decrease in the Hc, probably because of the decrease in the number of single-domain ferromagnetic particles.

An X-ray diffraction examination showed that the ferromagnetic samples consisted of crystalline particles with a disordered spinel structure(β-$LiFe_5O_8$).[9] This indicates that the formation of β-$LiFe_5O_8$ proceeded at the temperatures where the β phase was unstable. The transformation between the α and β phases of the samples as a result of heat treatment in air was confirmed from the experimental results, where their structure remained unchanged upon rapid cooling from 900 °C, whereas it was transformed into an ordered spinel structure (α-$LiFe_5O_8$) by slow cooling from 750 °C (Fig. 6). Such heat-treated samples consisted of the spinel phase with or without the α-Fe_2O_3 phase; the content of α-Fe_2O_3 varied with the sample. Decreasing the D of the original samples from 15 to 8 nm caused a slight increase (to several %) in the content of α-Fe_2O_3, while a further decrease in the D to 4.7 nm resulted in an increase to 50% in its content. The formation of α-Fe_2O_3 by heat treatment indicates that the Li-ion content in the original sample was less than that in $LiFe_5O_8$. According to the chemical analysis by the use of inductively coupled plasma/atomic emission spectroscopy, the β-$LiFe_5O_8$ samples with $D > 15$ nm contained Li and Fe ions in the atomic ratio (Li/Fe) of 0.2. This ratio decreased to 0.10 with the decrease in the D to 4.7 nm (Sample A).

In conclusion, the extremely fine particles, intermingled with ferromagnetic cubic particles, consisted of superparamagnetic and ferromagnetic particles. The superparamagnetic particles with vacancies of the Li ion slowly grew to ferromagnetic particles, and the composition approached $LiFe_5O_8$ when the D increased.

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