

On preparation of fine particles of MnFe_2O_4 and their magnetic properties

S N DOLIA, ANJALI KRISHNAMURTHY, BIPIN K SRIVASTAVA
and VIPASHA GHOSE

Department of Physics, University of Rajasthan, Jaipur 302004, India

MS received 2 March 1991; revised 19 November 1991

Abstract. Influence of the heat treatment, following a wet chemical process, has been examined on the sizes of the obtained particles of MnFe_2O_4 . X-ray diffraction, magnetization and Mössbauer measurements have been used. The average sizes of the obtained particles are in the range of $\sim 100 \text{ \AA}$ – 300 \AA with the upper size limit being $\sim 450 \text{ \AA}$ and more. The average size as well as size distribution is strongly influenced by the nature of the heat treatment followed for preparation of the sample. Prolonged hydrothermal heating resulted in larger average size than did dry heating at 400°C of the precipitate obtained from the initial wet process. Further dry heating following hydrothermal treatment did not lead to any major growth. Chemical nature of the starting materials also affects the sizes.

Keywords. Fine particle systems; ferrimagnetics.

PACS Nos 75-50; 75-60

1. Introduction

To prepare fine particles of spinel ferrites in particular, and magnetic oxides in general, apart from the technique of thermal precipitation from silicate or other glasses or crystalline materials (e.g. Komatsu and Soga 1980; Jamthe *et al* 1988; Dolia *et al* 1990), the wet chemical process of co-precipitation has been in wide use (e.g., Schuele and Deetscreek 1961; Morrish and Haneda 1981; Vandenberghe *et al* 1982; Komatsu and Soga 1984). In this process the growth of particle sizes is obtained by hydrothermal treatment. Taking MnFe_2O_4 as example, we have studied the wet chemical process followed with a course of heat treatment, involving hydrothermal and/or open atmosphere heating of the dried precipitate to examine its effect on the resulting particle size distributions. X-ray diffraction, initial susceptibility, coercive force and remanence data obtained from dc magnetization measurements and room temperature Mössbauer spectra have been used for characterization and to know about the particle sizes and their distribution. The results are compared with literature reports.

2. Experimental details

Wet chemical process has been followed using 3N grade pure $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and NaOH as the starting materials. The chlorides were dissolved in distilled water and mixed in the molar proportion 1:2. Likewise, NaOH in amount

proportional to 8 molar weight was dissolved in boiling distilled water. The two solutions were mixed with stirring and maintaining the temperature at $\sim 60^\circ\text{C}$ for about one hour. Subsequent to this three different thermal treatments were given. (1) Part of the mixture solution was put to filtering. The sodium chloride content in the resulting precipitate was washed out with distilled water with its absence being confirmed by AgCl test. The dried precipitate, which did not show any peak in X-ray diffraction, was heated in open atmosphere at 400°C for six hours and the sample obtained is termed as sample A. (2) Remaining part of the initial 60°C heated solution was subjected to further heating in a reflex condenser at boiling temperature for 100 h. The resulting precipitate was filtered and the sodium chloride was washed out. This sample is termed as sample B. (3) Separate amounts of part of the dried sample B—the one obtained by hydrothermal heating of original mixture solution—were heated in open atmosphere at 400°C for 48 h, at 500°C for 6 h and at the same temperature (500°C) for 10 h. These samples are referred to as samples C1, C2 and C3 respectively.

Powder X-ray diffraction patterns have been recorded on the Philips make diffractometer PW 1840 using FeK_α radiation. DC magnetization on powdered materials was measured on a Princeton Applied Research Co. make vibrating sample magnetometer model 155. For temperature dependent measurements a conventional high temperature oven was used. ^{57}Fe Mössbauer data at room temperature were recorded in constant acceleration mode in transmission geometry.

3. Results and discussion

The room temperature X-ray diffraction (XRD) patterns of the prepared samples, confirmed the formation of MnFe_2O_4 spinel phase. The XRD lines of the samples are quite broad suggesting the particle sizes to be rather small. Figure 1 shows (311) reflection for the five samples along with the 36° line of the bulk particle sized silicon specimen. It is noticed that the XRD line width, and hence the particle sizes, for the samples B and C1 are almost the same and likewise there is little difference between samples C2 and C3. Hence for further work from among the three samples of the 'boiled and dry heat treated' category, we pick only sample C3. Now, the XRD line width and particle size are connected through the Scherrer equation (Cullity 1956):

$$t = \frac{0.9\lambda}{B \cos \theta_B} \text{ with } B^2 = B_a^2 - B_b^2$$

where t is particle diameter, λ the wavelength of the X radiation, B a measure of the broadening of diffraction line due to size effect, B_a and B_b are the full widths at half maxima of the XRD line of the sample and of a standard specimen (of bulk-sized particles) respectively at around same Bragg angle and θ_B is the Bragg angle. Using this relation the particle sizes for the three samples, A, B and C3, have been estimated to be 60 \AA , 130 \AA and 160 \AA respectively (cf. Table 1).

Spinel ferrites in this size range, as in the samples under study, would show superparamagnetic (SPM) behaviour (Jamthe *et al* 1988; Mørup 1983). In fact room temperature Mössbauer spectra of the three samples, displayed in figure 2, showing co-existence of magnetically split and non-magnetic patterns in the centre, demonstrate their SPM behaviour.

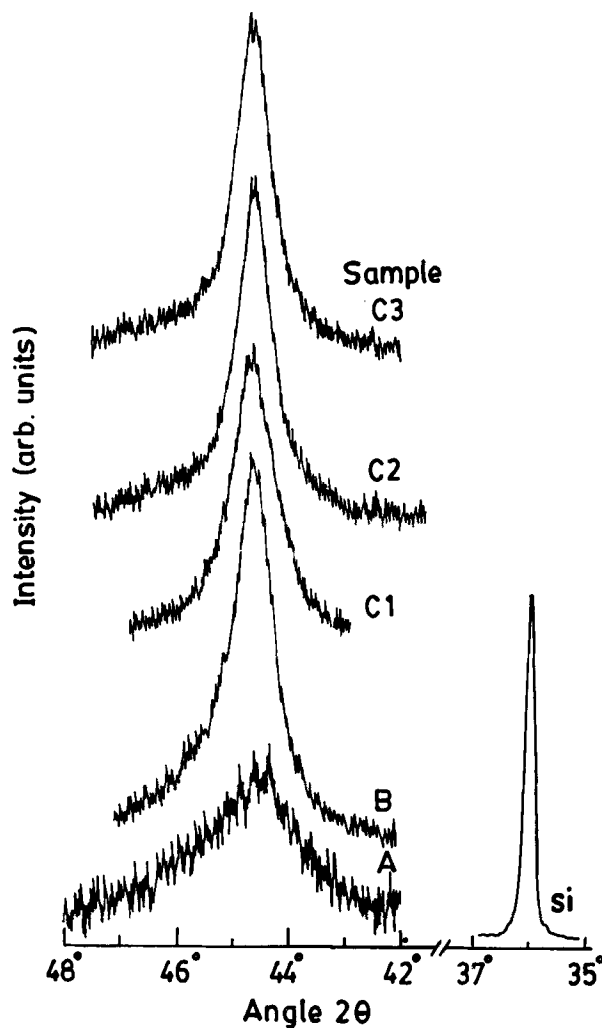


Figure 1. X-ray diffraction peak, recorded at room temperature using FeK_{α} radiation, corresponding to the (311) reflection of the five cubic spinel samples (cf. text). Peak at $2\theta = 36^{\circ}$ for the bulk particle sized standard specimen of Si is also shown.

Now for SPM particles the sizes can also be estimated through initial magnetic susceptibility (Yafet and Kittel 1952) using the relation

$$\frac{M}{H} = \frac{4\pi M_s^2 r^3}{9kT}$$

where M/H is the susceptibility, r the particle radius assuming spherical shape, M_s the saturation magnetization, T the temperature of measurement and k the Boltzmann constant. The estimated particle sizes, using the obtained initial susceptibility values and reported $M_s = 112 \text{ emu/g}$ (Krupicka and Novak 1987), as given in table 1, are 150 \AA , 330 \AA and 300 \AA respectively for the samples A, B and C3. These estimates are of the same order as from XRD line broadenings even though on the higher side.

Figure 3 shows $M-H$ loop at different temperatures, for the sample A as a typical example. Insets show expanded plots in small field region from which the coercivity

Table 1. Average particle sizes and the magnetization data for the three prepared samples of MnFe_2O_4 .

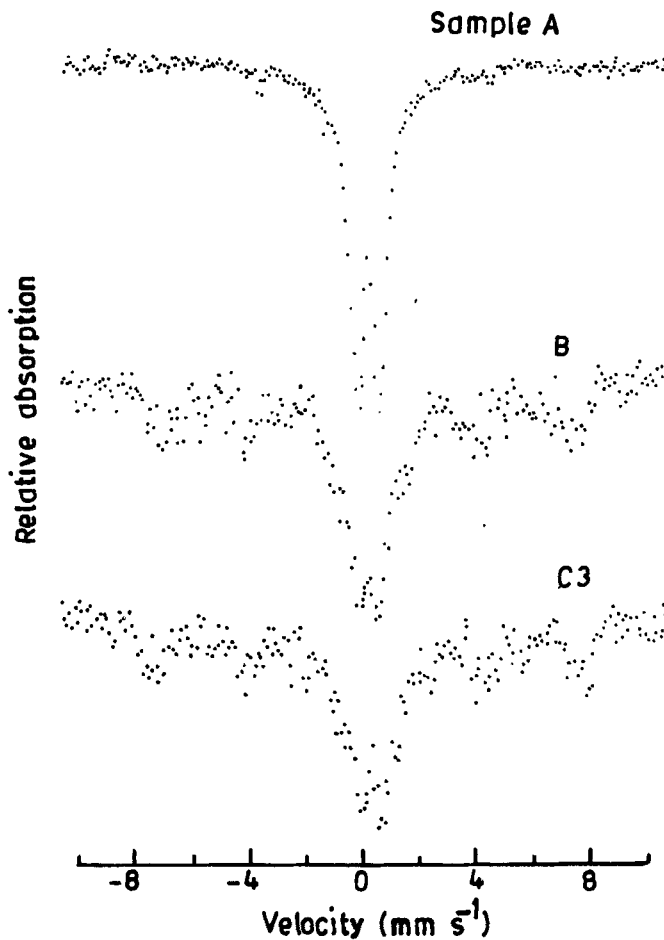
Sample*	Particle Size (\AA) ⁺		M_s^{**} (emu/g)	T^{++} (K)	H_c^{++} (Oe)	M_r^{++} (emu/g)
	XRD	χ				
A	60	150	8	90	180	1.4
				300	45	0.6
				400	15	0.2
				500	3	0.05
B	130	330	50	90	100	6.8
				300	10	1.2
				500	5	0.4
C3	160	300	40	90	200	8.0
				300	30	2.0
				500	~ 0	~ 0

*For nomenclature of samples, please see text.

⁺ Average sizes estimated using X-ray diffraction (XRD) line broadening and initial susceptibility (χ) are given in different columns.

** M_s is magnetization measured at 5 kOe and at 90 K.

⁺⁺ Coercivity (H_c) and remanence (M_r) at different temperatures.

**Figure 2.** ^{57}Fe Mössbauer spectra of three samples (cf. text) at room temperature.

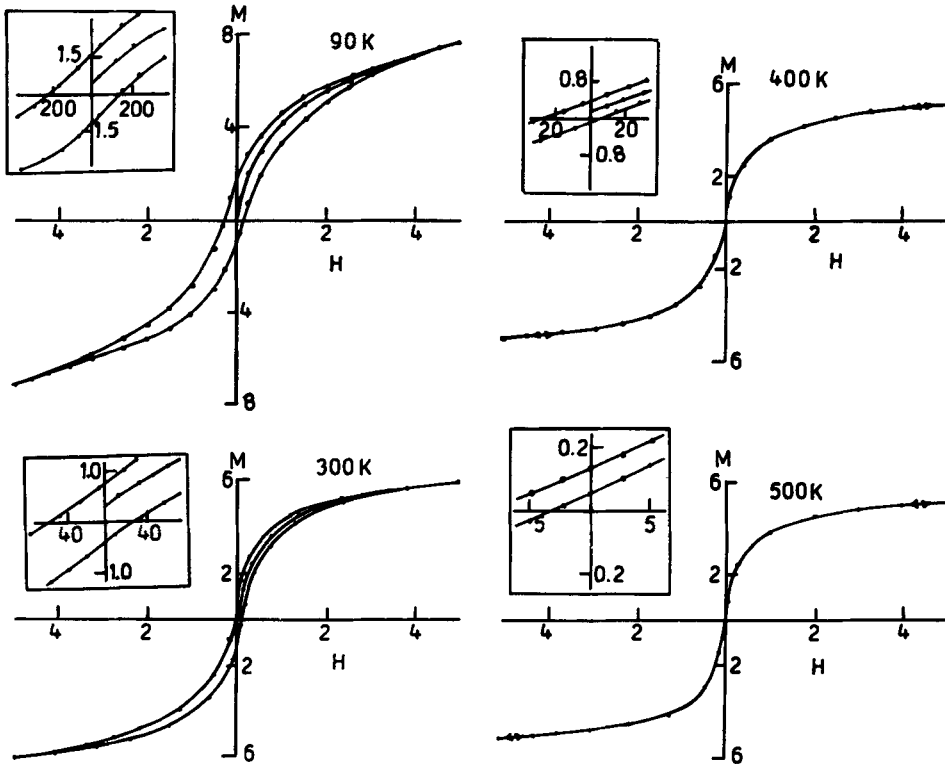


Figure 3. $M(\text{emu/g})$ - $H(\text{kOe})$ loop for the sample A (cf. text) recorded at four temperatures. Insets show expanded plots in small field (in Oe) region.

H_c and remanence M_r have been obtained. Figure 4 shows plots of H_c and M_r as a function of temperature. A continuous decrease is observed in both H_c and M_r values with increasing T . Bean (1955) obtained similar curves on plotting H_c versus volume fraction of low coercive material in mixtures of SPM and larger single domain particles. Reported results on mixtures of cobalt particles supported Bean's observations (Meiklejohn 1953). Now increasing the temperature of a given sample with distributed particle sizes is equivalent to increasing the fraction of SPM part in the sample. Thus our results on H_c variation with T suggest particles in each of these samples to have distributed sizes.

Further, it is found that the fall in H_c in going from 90 K to 300 K is steeper in the sample B than in C3 and A. M_r values show a similar trend. Then in going from 300 K to 500 K, H_c and M_r values show the steepest fall in sample C3 and the least in sample B. These observations would suggest that in the lower size domain, sample B has the narrowest size distribution with samples C3 and A having wider distributions in the increasing order. In the larger size domain, sample C3 should have the narrowest and B the widest distribution. Such size distributions would also explain the larger value of susceptibility estimated size in sample B than in sample C3 even though XRD line broadening estimates are the other way round.

Now comparing H_c values of different samples, we note that at 300 K, it is much lower for sample B (10 Oe) than for sample A (45 Oe) although the average particle sizes of these two samples are the other way round. This would imply that sample B

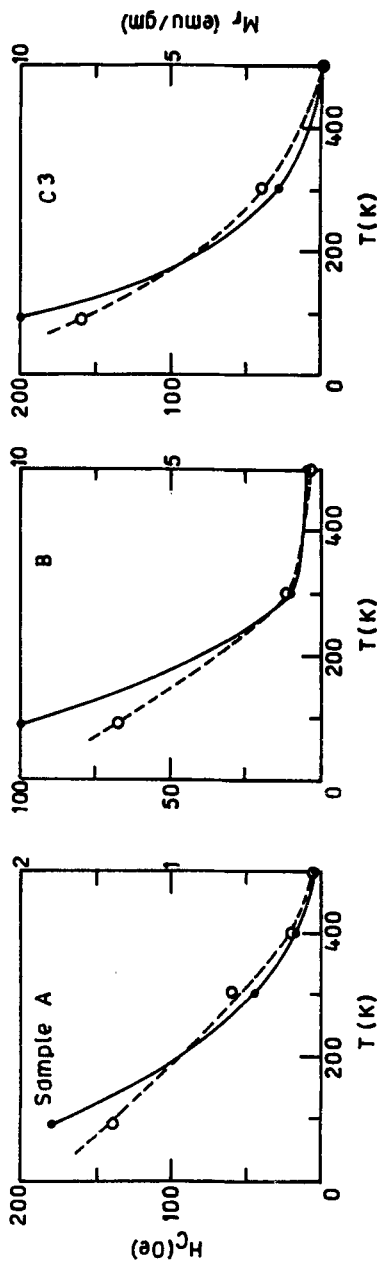


Figure 4. Coercivity (H_c , —●—) and remanence (M_r , -○-) as a function of temperature for three samples (cf. text).

contains large fraction of particles of sizes greater than that of single domain ones. It may be noted that for magnetite and also $NiFe_2O_4$ the critical size for single domain pseudo-single domain boundary has been reported to be $\sim 300 \text{ \AA}$, viz., in the same size region as encountered here.

Further, for sample C3, H_c at 300 K is greater than for sample B again suggesting a narrower distribution of sizes in the higher size region for this sample, as discussed above. In this sample, both H_c and M_r are ~ 0 at 500 K. Now relaxation time is given as (Néel 1948) $\tau = f_0^{-1} \exp(KV/kT)$ where f_0 is a frequency factor $\sim 10^9 \text{ s}^{-1}$, K is magnetic anisotropy constant, V the volume and kT the thermal energy. Taking observation time $\tau_0 \sim 1 \text{ s}$ and $K = 4.0 \times 10^4 \text{ erg cm}^{-3}$ (Krupicka and Novak 1987) for $MnFe_2O_4$ this relation gives, corresponding to a blocking temperature $T = 500 \text{ K}$, an upper limit of $\sim 400 \text{ \AA} - 450 \text{ \AA}$ for the particle sizes. Samples B and A would contain particles of larger sizes as well.

Vandenberghé *et al* (1982) reported their results on the $MnFe_2O_4$ particles produced by wet chemical process beginning with nitrates, instead of chlorides, as the starting materials, and followed with only hydrothermal treatment. Comparison shows that the obtained particle sizes in the two studies, viz. Vandenberghé *et al* and ours, are in the same range. However, our values (at 300 K) of 40 emu/g (50 emu/g at 90 K) and 1.2 emu/g for M_s and M_r for 130 \AA average particle sized sample B are somewhat higher than the values of 26 emu/g and 0.26 emu/g respectively reported by Vandenberghé *et al* for the 147 \AA average particle sized sample. This may suggest that use of chlorides as against nitrates as starting materials results in a broader distribution.

It is also to be noted that after hydrothermal treatment, the open atmosphere heating results in only slight growth in particle sizes. In fact dry heating, at 400°C, of sample B does not at all contribute to growth in size and dry heating at 500°C leads to only a little growth as shown by figure 1. More revealing is the fact that open atmosphere dry heating preceded by hydrothermal heating leads to narrower distribution in the larger size domain than does only hydrothermal treatment over a prolonged time.

References

- Bean C P 1955 *J. Appl. Phys.* **26** 1381
Cullity B D 1956 *Elements of X-ray diffraction* (Massachusetts, USA: Addison Wesley) p. 352
Dolia S N, Krishnamurthy A and Srivastava B K 1990 *Indian J. Pure Appl. Phys.* **28** 464
Jamthe N M, Krishnamurthy A and Srivastava B K 1988 *Indian J. Pure Appl. Phys.* **26** 333
Komatsu T and Soga N 1980 *J. Appl. Phys.* **51** 801
Komatsu T and Soga N 1984 *J. Mater. Sci.* **19** 2353
Krupicka S and Novak P 1987 in *Ferromagnetic materials* (ed.) E P Wohlfarth (Netherlands: North-Holland Publishing) Vol. 3, 291, 296
Meiklejohn W H 1953 *Rev. Mod. Phys.* **25** 302
Morrish A H and Haneda K 1981 *J. Appl. Phys.* **52** 2496
Mørup S 1983 *J. Magn. Magn. Mater.* **37** 39
Néel L 1948 *Ann. Phys. (Paris)* **3** 137
Schuele W J and Deetscreek V D 1961 *J. Appl. Phys.* **32** 2355
Vandenberghé R E, Vandenberghé R and Robbrecht G G 1982 *Solid State Chem.* **3** 395
Yafet Y and Kittel C 1952 *Phys. Rev.* **87** 290