Comparison of Magnetic Properties of MgFe₂O₄ Prepared by Wet-Chemical and Ceramic Methods

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The magnetic properties of magnesium ferrite (MgFe₂O₄) prepared by a wet-chemical method and by a ceramic method have been investigated by means of Mössbauer spectroscopy, susceptibility, and magnetization measurements. The temperature dependence of the Mössbauer spectra has shown the existence of superparamagnetic clusters in the MgFe₂O₄ sample prepared by the wet-chemical method and this is confirmed by observing a maximum in the low-field ac susceptibility versus temperature measurements. On the other hand, the ceramic preparation exhibits relaxation behavior at high temperatures. It is found that high temperature annealing of the MgFe₂O₄ prepared by a wet-chemical method gives the properties close to that obtained with the usual ceramic method. These observations suggest that the magnetic properties depend on the particular method of preparation. © 1986 Academic Press, Inc.

Introduction

The method of preparation plays a very important role with regard to the chemical, structural, and magnetic properties of a spinel ferrite. Ferrites synthesized by two different methods have been found to exhibit different properties mentioned above (*1*).

The magnesium ferrite (MgFe₂O₄) possesses a partially inverse spinel structure. This ferrite has been prepared by the ceramic method and extensively studied by a number of workers (*2, 3*). Material of the same composition (MgFe₂O₄) but with very different properties can be prepared at lower temperatures by co-precipitation from aqueous solutions of the corresponding hydroxides (wet-chemical method) (*4*). Moreover, after high-temperature annealing the properties of the wet-chemically prepared MgFe₂O₄ become very close to

that obtained with the usual ceramic method. No measurements have been reported on wet-prepared magnesium ferrite.

The aim of the present work is to prepare MgFe₂O₄ by wet-chemical and ceramic methods and to study the structural and magnetic properties of the products. The magnetic properties at different temperatures were investigated by means of Mössbauer spectroscopy and the low-field ac susceptibility measurements. X-ray diffractometry was employed to determine the crystal structure.

Experimental

The ceramic sample of MgFe₂O₄ was prepared by mixing analytical reagent grade Fe₂O₃ (Robert & Johnson) and MgO (E. Merck) in stoichiometric proportions fired at 1100°C for 48 hr and slowly cooled to room temperature.

The wet sample of $MgFe_2O_4$ was prepared by air oxidation of an aqueous suspension containing the Mg^{2+} and Fe^{2+} ions in $1:2$ ratio. The starting solution was prepared by mixing 50 ml of aqueous solutions of $FeSO_4 \cdot 7H_2O$ (0.25 M) and $MgSO_4 \cdot 7H_2O$ (0.125 M). A solution containing 80 g of NaOH in 1000 ml of water was prepared as a precipitant. For simultaneous precipitation (5) of both the hydroxides, $Mg(OH)_2$ and $Fe(OH)_2$, the starting solution (pH value about 3) was added to the solution of NaOH and a suspension (pH 9.29) containing green intermediate precipitates was formed. Then the suspension was heated and kept at a temperature 55°C, while air was bubbled uniformly in to the suspension to stir it as well as to promote oxidation reaction until all the intermediate precipitates changed into the dark brownish precipitates of the spinel ferrite. The sample was filtered, washed and dried at 150°C under vacuum.

The wet sample of $MgFe_2O_4$ was annealed in air at 1100°C for 24 hr. After high-temperature annealing, the wet sample exhibits weight loss around 2% because of removal of water and hydroxyl ions absorbed or chemically combined even after the drying process.

The composition of the wet sample was checked by chemical analysis. (Found: Mg, 11.8%; Fe, 55.6%. Calc: Mg, 12.2%; Fe, 55.9%).

The X-ray powder patterns were recorded using FeK_α radiation on a Philips (PM 9920) diffractometer. The saturation magnetization of each sample was carried out using the high-field hysteresis loop techniques. The low-field ac susceptibility measurements on powdered samples were made in the temperature range 300–800 K using double-coil setup (6) operating at a frequency of 263 Hz and in the rms field of 5.0 Oe.

The Mössbauer absorbers were made using samples in the powder form of thickness between 20 to 30 mg $\cdot$ cm^{-2}. The Mössbauer spectra were obtained with a constant acceleration transducer and a 256 multichannel analyzer operating in the time mode. A γ source of $^{57}Co(Pd)$ of 10 mCi was used. All the spectra were obtained within the temperature range 300–750 K in the transmission geometry and 14.4 keV γ rays were detected with a xenon-methane filled proportional counter. The temperatures of the absorbers were measured with a Chromel-alumel thermocouple. The solid lines through the data points in Figs. 1, 3, 4, 5 are the results of the least-squares fits of the data.

Results and Discussion

The X-ray diffraction patterns showed that all the samples were single-phase spinels. No amorphous phase has been detected. The lattice constants found from the X-ray powder diffractometry patterns for all the samples are listed in Table I. The wet-prepared $MgFe_2O_4$ is characterized by a smaller lattice constant than that of the ceramic-prepared $MgFe_2O_4$. After high-temperature annealing the lattice constant of the wet $MgFe_2O_4$ is found to be increased.

The room temperature Mössbauer spectra of wet, ceramic, and annealed samples of $MgFe_2O_4$ are shown in Fig. 1 and the

TABLE I

LATTICE CONSTANT (a), SATURATION MAGNETIZATION (σ_s),[a] AND NEEL TEMPERATURE (T_N) FOR $MgFe_2O_4$

$MgFe_2O_4$	a (Å)	σ_s (emu/g) at 298 K	T_N (K) Suscept.	T_N (K) Mössbauer
Ceramic	8.367 ± 0.002	27	715 ± 3	703 ± 5
Wet	8.323 ± 0.002	22	753 ± 3	733 ± 5
Annealed	8.354 ± 0.002	25	730 ± 3	720 ± 5

[a] Error 3%.

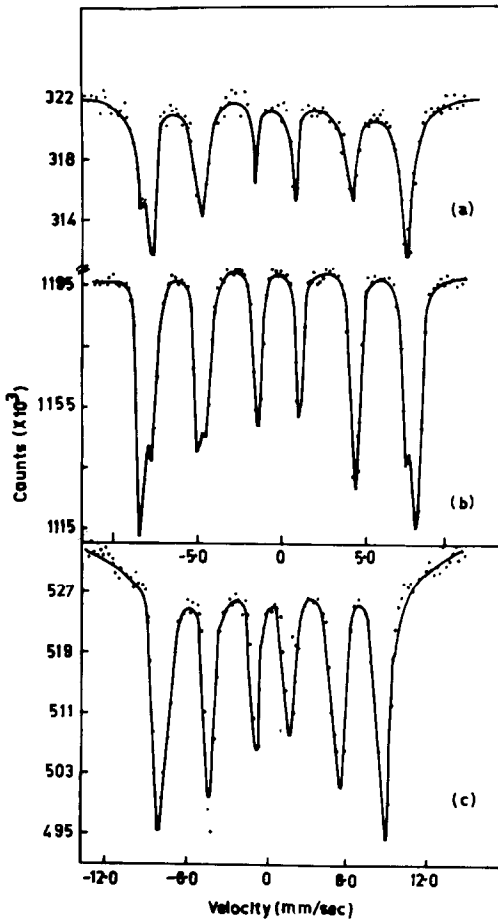FIG. 1. Mössbauer spectra at room temperature of MgFe$_2$O$_4$. (a) Wet sample; (b) wet sample annealed at 1100°C in air; and (c) ceramic sample.

Mössbauer data at 300 K are summarized in Table II. By means of Mössbauer results of MgFe$_2$O$_4$, the cation distribution has been found to be $(\mathrm{Mg}_{1-x}^{2+}\mathrm{Fe}_x^{3+})^A[\mathrm{Mg}_x^{2+}\mathrm{Fe}_{2-x}^{3+}]^BO_4^{2-}$, where ions enclosed by the parentheses correspond to the tetrahedral (A) site and the ions enclosed by the brackets correspond to the octahedral (B) site. It is evident from Table II that the low-temperature preparation (i.e., wet-chemical method) increases the degree of inversion (x) in the MgFe$_2$O$_4$ structure.

The smaller value of the lattice constant for wet MgFe$_2$O$_4$ cannot be explained only on the basis of the degree of inversion (x). This may also be due to the different degrees of crystallinity of the wet- and ceramic-prepared samples resulting from the differences in the temperatures of crystallinity.

The X-ray diffraction lines were slightly broad in the case of wet-prepared MgFe$_2$O$_4$ because of the particle size effect. The average particle size determined from the full width at half maxima of the diffraction lines for wet MgFe$_2$O$_4$ was around 500 Å. The X-ray diffraction lines of the annealed wet sample and of the ceramic sample were sharp. This indicates that the high-temperature annealing of the wet MgFe$_2$O$_4$ has increased the crystallite size up to the order of a ceramic ferrite.

The lower value of the saturation magne-

TABLE II

THE ISOMER SHIFT(IS),[a] QUADRUPOLE SPLITTING(QS), HYPERFINE FIELD(H) AND DEGREE OF INVERSION (x) DEDUCED FROM MÖSSBAUER SPECTRA OF FIG. 1

| MgFe$_2$O$_4$ | IS(mm/sec) | | QS(mm/sec) | | H^b(kOe) | | |
	IS(B)	IS(A)	QS(B)	QS(A)	H_B	H_A	x
Ceramic	0.38 ± 0.02	0.31 ± 0.02	0.00 ± 0.03	0.00 ± 0.03	511	490	0.80 ± 0.01
Wet	0.32 ± 0.02	0.27 ± 0.03	0.16 ± 0.03	0.11 ± 0.03	482	503	0.92 ± 0.01
Annealed	0.34 ± 0.03	0.30 ± 0.02	0.00 ± 0.03	0.00 ± 0.03	505	477	0.85 ± 0.01

[a] With respect to iron metal.
[b] Error in H is ±3 kOe.

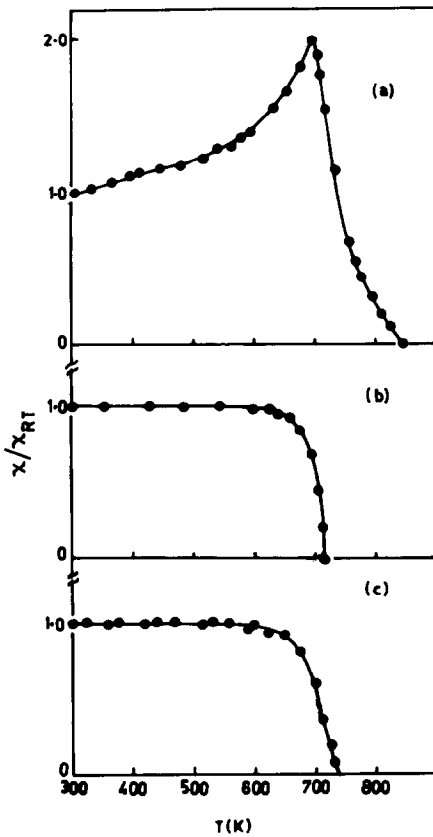FIG. 2. Temperature dependence of low-field ac susceptibility of $MgFe_2O_4$. (a) Wet sample; (b) ceramic sample; and (c) wet sample annealed at 1100°C in air.

tization for a wet sample compared to the ceramic and annealed samples of $MgFe_2O_4$ (Table I) is due to stronger covalency effects arising from smaller cationic site dimensions. Moreover, according to colinear spin arrangement the net magnetic moment of wet $MgFe_2O_4$ is expected to be low because of higher degree of inversion compared to the ceramic and annealed samples.

The temperature dependence of the ac susceptibility for the wet, ceramic, and annealed samples of $MgFe_2O_4$ is shown in Fig. 2. It is apparent from Fig. 2 that the susceptibility cusp is well pronounced for wet-prepared $MgFe_2O_4$. It has been suggested (7) that humps or cusps in $\chi_{ac} - T$ curves indicate the presence of a single domain (SD)

in a sample and lack of such features imply that the sample consists predominantly of multidomain (MD) grains. The shape of the $\chi_{ac} - T$ curve (Fig. 2b) for ceramic $MgFe_2O_4$ indicates that the sample contains a predominantly multidomain grains. The observed sharp susceptibility maximum for wet $MgFe_2O_4$ may be either attributed to single domain-superparamagnetic (SD-SP) transition or to a cluster spin glass type of ordering. But our high-temperature Mössbauer spectra (Fig. 3) of wet sample rule out the possibility of spin glass type of or-
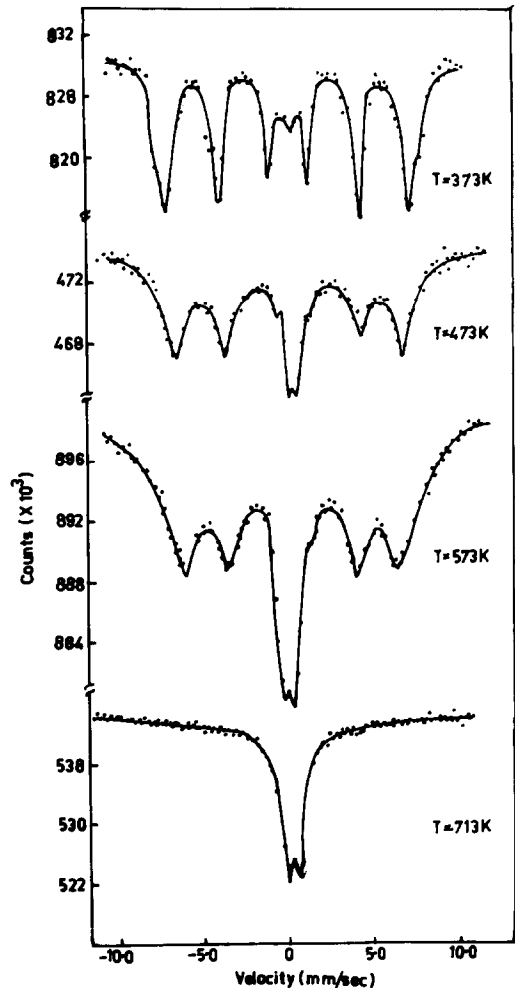

FIG. 3. Temperature dependence of the Mössbauer spectra of wet $MgFe_2O_4$.

dering and support the superparamagnetic clustering behavior. It is evident from Fig. 2c that a high-temperature annealing of the wet sample changes it in to the multidomain state of a ceramic ferrite. The Neel temperatures obtained from Fig. 2 agree well with the Neel temperatures determined by the Mössbauer measurements (Table I).

The temperature dependence of Mössbauer spectra for wet and ceramic $MgFe_2O_4$ samples are shown in Figs. 3 and 4, respectively. The Mössbauer parameters determined from these spectra are given in Tables III and IV. The reported Mössbauer spectra (Fig. 3) of wet $MgFe_2O_4$ clearly indicate that the magnetically ordered regions and superparamagnetic clusters are simultaneously present and the presence of superparamagnetic clustering enhances as the temperature is increased towards the Neel temperature (T_N). These observations are in very good agreement with our low-field ac susceptibility measurements. This confirms that the observed cusp in $\chi_{ac} - T$ curve is definitely due to superparamagnetic clustering. On the contrary, the Mössbauer spectra (Fig. 4) of ceramic $MgFe_2O_4$ exhibits relaxation behavior at $T = 573$ K and
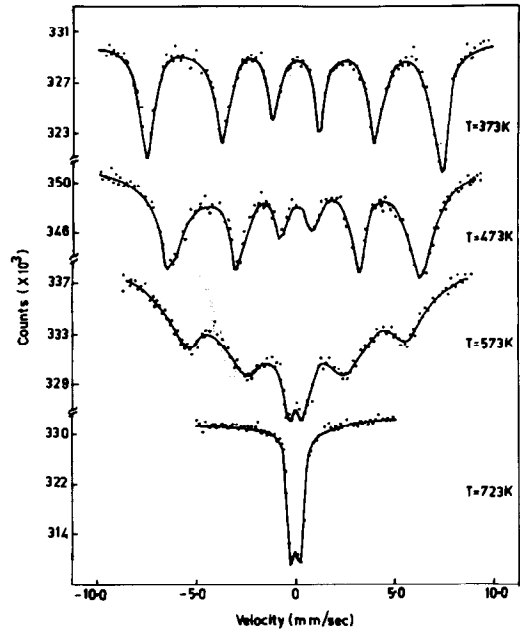

Fig. 4. Temperature dependence of the Mössbauer spectra of ceramic $MgFe_2O_4$.

these observations are in confirmity with the susceptibility measurements. This indicates that in the wet-prepared $MgFe_2O_4$ the relaxation of the magnetically ordered re-

TABLE III

Temperature Dependence of Isomer Shift(IS),[a] Quadrupole Splitting(QS), and Hyperfine Field(H) for Wet $MgFe_2O_4$

T(K)		IS(mm/sec)		QS(mm/sec)		H^b(kOe)	
		IS(B)	IS(A)	QS(B)	QS(A)	H_B	H_A
373	I[c]	0.34 ± 0.02	0.31 ± 0.03	0.19 ± 0.02	0.17 ± 0.02	464	491
	II	0.18 ± 0.03	—	—	—	—	—
473	I	0.37 ± 0.02	0.33 ± 0.02	0.22 ± 0.02	0.20 ± 0.03	445	466
	II	0.28 ± 0.02	—	0.36 ± 0.03	—	—	—
573	I	0.40 ± 0.02	0.38 ± 0.02	0.23 ± 0.02	0.21 ± 0.02	413	442
	II	0.29 ± 0.02	—	0.51 ± 0.02	—	—	—
713	I	—	—	—	—	—	—
	II	0.35 ± 0.02	—	0.68 ± 0.03	—	—	—

[a] With respect to iron metal.
[b] Error in H is ±3 kOe.
[c] I, sextets; II, central doublet.

TABLE IV

TEMPERATURE DEPENDENCE OF ISOMER SHIFT(IS),[a] QUADRUPOLE SPLITTING(QS), AND
HYPERFINE FIELD(H) FOR CERAMIC $MgFe_2O_4$

T(K)	IS(mm/sec)		QS(mm/sec)		H^b(kOe)	
	IS(B)	IS(A)	QS(B)	QS(A)	H_B	H_A
373	0.35 ± 0.03	0.28 ± 0.02	0.00 ± 0.06	0.00 ± 0.06	453	441
473	0.30 ± 0.02	0.25 ± 0.03	0.00 ± 0.06	0.00 ± 0.06	359	355
573			Relaxation spectrum			
723	0.21 ± 0.02	—	0.42 ± 0.06		—	—

[a] With respect to iron metal.
[b] Error in H is ±3 kOe.

gions seems to be hampered by the presence of the magnetically isolated clusters.

The Mössbauer characterization of annealed wet sample is shown in Fig. 5 at T = 473 and 573 K. The Mössbauer spectrum of an annealed wet sample at T = 573 K exhibits relaxation behavior. No central doublet was observed in the Mössbauer spectra of an annealed sample at T = 473 and 573 K. This suggests that after high-temperature annealing the wet $MgFe_2O_4$ transforms in to the ordered magnetic structure and exhibits ceramic-type properties.

It is interesting to note that the H_A is

FIG. 5. High-temperature Mössbauer spectra of wet $MgFe_2O_4$ after annealing at 1100°C in air.

greater than H_B for wet prepared $MgFe_2O_4$ (Table II). This is attributable to the stronger covalency effects at the smaller cationic site dimensions. It is clear from Table III that H_A and H_B vary slowly with temperature. On the other hand, for ceramic-prepared $MgFe_2O_4$ (Table IV) H_B is greater than H_A and both the hyperfine fields H_A and H_B vary considerably with temperature. At room temperature the smaller values of isomer shift for wet $MgFe_2O_4$ (Table II) are also due to covalency effects. It is clear from Tables III and IV that the isomer shifts, IS(A) and IS(B), for wet $MgFe_2O_4$ increase with temperature, whereas for ceramic $MgFe_2O_4$ they decrease with temperature. The quadrupole splittings, QS(A) and QS(B), increase with temperature for wet $MgFe_2O_4$. In the case of ceramic $MgFe_2O_4$, no quadrupole splitting was observed for magnetically split spectra but it was observed in the paramagnetic doublet (Table IV). This suggests that the co-existence of chemical disorder and overall cubic symmetry causes no net observable quadrupole shifts in the Zeeman sextets (8).

It is believed that these results are related to the preparation conditions. The low-temperature synthesis of the wet-prepared $MgFe_2O_4$ leads to the disordered system (i.e., simultaneous presence of magnetically ordered regions and superpara-
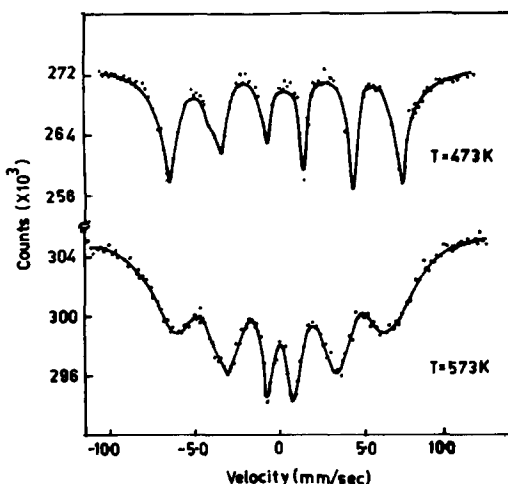
magnetic clusters) and high-temperature annealing changes the wet MgFe$_2$O$_4$ in to the ordered magnetic structure of the ceramic ferrite.

Acknowledgments

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