Magnetic properties, compositions, and microstructures of high-energy product strontium hexaferrites

G. K. Thompson and B. J. Evans

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

Commercial, high-energy product strontium hexaferrites have been characterized in terms of their chemical compositions, microstructures, and bulk and submicroscopic magnetic properties. Compared to earlier permanent magnetic hexaferrites, these materials have a unique composition, containing no elements other than Sr and Fe at appreciable concentrations; dopants for nucleation and microstructure control are apparently absent. The microstructures indicate that, in some cases, the materials may be fully reacted prior to forming the final ceramic bodies. The compositions are variable and tend to be nonstoichiometric despite the absence of impurity elements. These deviations from stoichiometry are reflected in the Mössbauer spectra which indicate that further refinements can be made in the definition of the different magnetic sublattices. These refinements may lead to further advances in the magnetic properties.

INTRODUCTION

High-energy product, commercial strontium hexaferrites with H_c between 3400 and 3200 Oe and B_r between 4000 and 3500 G, respectively, have been noted recently and evaluated for motor applications.¹ Further improvements in magnetic properties have been made, and strontium ferrites with $H_c \geq 4 \times 10^3$ Oe, $B_r \geq 4 \times 10^3$ G, and $(BH)_{\max} \geq 4$ MGOe are now commercially available. These properties rival those of the best laboratory materials.^{2,3} In view of the materials and processing cost, it would, however, be surprising if the commercial samples closely resembled the laboratory ones in terms of their chemical composition. Therefore, in order to understand the basis of their superior magnetic properties, several commercial strontium hexaferrite permanent magnet materials have been investigated by means of x-ray powder diffraction, wet-chemical analysis, scanning electron microscopy and electron microprobe analyses, and ^{57}Fe Mössbauer spectroscopy and magnetization measurements.

These measurements reveal that these new materials differ from traditional ones in that strontium and iron are the only metals present in appreciable concentrations, indicating the starting materials to be of higher purity than reagent-grade laboratory chemicals. Both wet-chemical analysis and Mössbauer spectroscopy demonstrate that some of these materials are not stoichiometric and that further improvements in magnetic properties may be achievable.

EXPERIMENT

Samples of strontium hexaferrite were obtained from the manufacturer and selected on the basis of technical data sheets which listed maximal B_r , H_c , and $(BH)_{\max}$ values of approximately 0.4 T, 4 kOe, and 4 MGOe, respectively. Four different samples have been investigated; no properties data on these particular specimens were obtained from the manufacturer. X-ray diffraction data were obtained by means of a powder diffractometer using copper $K\alpha$ radiation. The chemical compositions of the samples were determined by means of electron microprobe, scanning electron microscopic, and wet-chemical analyses. The textures of the samples were determined by means of a scanning electron

microscope. ^{57}Fe Mössbauer spectra were obtained and analyzed as described in detail in an earlier report.² Magnetization measurements were performed on spherical samples by means of a commercial SQUID susceptometer. Calibrations were performed with a sphere of high-purity nickel.

RESULTS

The chemical compositions determined in this investigation are given in Table I. The data reported are the average of several analyses. It is believed that the wet-chemical analyses are superior to the electron microprobe analyses, but it is clear that, irrespective of the method of analysis, some samples deviate significantly from the 1:12 strontium-to-iron ratio of the magnetoplumbite structure. A typical powder diffraction pattern is shown in Fig. 1: No lines other than those for the magnetoplumbite structure were observed despite the deviation from ideal stoichiometry (cf. Table I). Slight differences in the degree of sintering for the four samples, as indicated by the coalescing of individual particles, were revealed by scanning electron microscopy. The presence of numerous hexagonal platelets with edge thicknesses

TABLE I. Chemical composition of commercial hexaferrite samples.

Sample No.	Average Fe weight percent	Average Sr weight percent	Fe:Sr (molar ratio)
18	61.2 ± 0.1^a	7.9 ± 0.1	12.2:1
	60.6 ± 0.6^b	8.1 ± 0.1	11.7:1
28	60.9 ± 0.1	8.3 ± 0.1	11.5:1
	60.3 ± 0.4	7.9 ± 0.3	12.0:1
29	57.4 ± 0.2	5.5 ± 0.1	16.3:1
	61.3 ± 0.5	7.6 ± 0.5	12.7:1
118	60.8 ± 0.2	6.4 ± 0.3	14.8:1
	61.2 ± 0.1	7.9 ± 0.1	12.2:1

^a The first entry for each sample is the results of analysis by wet-chemical methods.

^b The second entry for each sample is the results of analysis by an electron microprobe analyzer.

FIG. 1. X-ray powder diffraction pattern of hexaferrite sample 118 obtained with Cu $K\alpha$ radiation. All of the lines can be ascribed to the magnetoplumbite strontium hexaferrite pattern.

of about $1\ \mu\text{m}$ is a remarkable feature of the microstructure that is pronounced in samples 28 and 29. The magnetic moment for sample 18 was $65.74\ \text{emu g}^{-1}$ at 298 K and $98.72\ \text{emu g}^{-1}$ at 10 K, both of which are somewhat lower than those obtained in previous measurements on well-characterized single crystals.⁴ ^{57}Fe Mössbauer spectra are shown in Fig. 2. The resolution for the different iron subspectra is considerably improved over that for commercial Sr-hexaferrites with lower H_c , B_r , and $(BH)_{\text{max}}$ (Ref. 5); five distinct subspectra are required to fit the data adequately. Parameters for the Mössbauer spectra of the four commercial samples are listed in Table II; the parameters obtained in this investigation for a high-purity $\text{SrFe}_{12}\text{O}_{19}$ sample that had

TABLE II. ^{57}Fe hyperfine parameters for hexaferrite samples at 298 K.

Iron site	Sample	H_{eff}^a (kOe)	δ^a (mm s^{-1})	Δ^a (mm s^{-1})	Relative intensity
12k	18	409	0.34	0.36	12
	28	407	0.34	0.36	12
	29	409	0.34	0.36	12
	118	409	0.34	0.36	12
	HiP ^b	410	0.33	0.36	12
4f ₁	18	492	0.12	0.21	5.7
	28	490	0.11	0.22	5.7
	29	490	0.13	0.18	4.9
	118	491	0.13	0.22	5.3
	HiP	493	0.20	0.35	4.8
4f ₂	18	517	0.38	0.28	4.7
	28	516	0.38	0.30	4.5
	29	516	0.38	0.28	5.1
	118	516	0.38	0.28	5.1
	HiP	518	0.36	0.32	4.0
2a	18	497	0.46	0.22	3.1
	28	496	0.46	0.24	3.1
	29	496	0.44	0.20	3.3
	118	497	0.45	0.20	2.7
	HiP	511	0.34	0.04	3.0
2b	18	409	0.29	2.18	1.9
	28	407	0.31	2.18	1.8
	29	408	0.31	2.18	1.9
	118	408	0.30	2.2	1.8
	HiP	408	0.29	2.2	1.7

^a Estimated errors in H_{eff} , δ (relative to Fe metal), and Δ are ± 4 kOe, $\pm 0.01\ \text{mm s}^{-1}$, and $\pm 0.05\ \text{mm s}^{-1}$, respectively.

^b HiP is for the high-purity $\text{SrFe}_{12}\text{O}_{19}$ sample described in an earlier report (Ref. 2).

been studied previously² are also included in Table II for comparison. Despite the high resolution of the spectra of these new materials, the five subspectra are not as clearly delineated as in high-purity, stoichiometric strontium hexaferrite, and the relative intensities of the different subspectra (cf. Table II) are quite different from the expected ones.²

CONCLUSIONS

A unique feature of the commercial hexaferrite samples investigated in this study is the absence of appreciable concentrations of elements other than strontium and iron. The achievement of large values of B_r , H_c , and $(BH)_{\text{max}}$ in the absence of foreign ions that could serve variously as "mineralizers," "sintering aids," etc., is in marked contrast to earlier manufacturing paradigms for permanent magnet hexagonal ferrites. In addition, the ceramic bodies consist of relatively small particles that have a hexagonal platelet morphology, which suggests that the powders used to form the ceramic body may have been well-crystallized hexagonal ferrites.

Despite the improved magnetic properties of these materials, some of the samples are nonstoichiometric. This nonstoichiometry is apparent in the degree of resolution and relative intensities of the ^{57}Fe Mössbauer subspectra of the various lattice sites. The nonstoichiometry correlates with the relative intensity of the pattern assigned to the $4f_2$ site. The low values for the saturation magnetization might also be reflective of the nonstoichiometries. Thus it is reasonable

FIG. 2. ^{57}Fe Mössbauer spectra of hexaferrite samples 18 and 29 at 298 K. The solid line represents a fit of five subspectra.

to expect that the saturation magnetization would increase for more stoichiometric samples, which could lead to further increases in B_s and $(BH)_{\max}$.

¹R. E. Tompkins, in *Advances in Ceramics*, edited by F. Y. Wang (American Ceramic Society, Columbus, OH, 1985), Vol. 16, Pt. II, p. 525.

²B. J. Evans, F. Grandjean, A. P. Lilot, R. H. Vogel, and A. Gérard, *J. Magn. Magn. Mater.* **67**, 123 (1987).

³C. A. M. van den Broek and A. L. Stuijts, *Philips Tech. Rev.* **37**, 157 (1977).

⁴B. T. Shirk and W. R. Bussem, *J. Appl. Phys.* **40**, 1294 (1969).

⁵R. H. Vogel and B. J. Evans, *J. Appl. Phys.* **49**, 1570 (1978).