

Solid state and magnetochemistry of the SrO-Fe₂O₃ system IV. Synthesis of SrFe₁₂O₁₉ from coprecipitated precursors^{a)}

Xueyu Qian and B. J. Evans

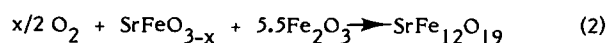
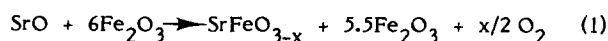
University of Michigan, Ann Arbor, Michigan 48109

By means of ⁵⁷Fe Mössbauer spectroscopy and powder x-ray diffraction techniques, it has been determined that the formation of SrFe₁₂O₁₉ from coprecipitated ferric hydroxide and strontium laurate follows a reaction mechanism different from that when SrCO₃ and Fe₂O₃ are used as starting materials. Upon heating at 300 °C in vacuum, strontium laurate decomposes and further heating to 550 °C leads to the formation of γ-Fe₂O₃ from the ferric hydroxide and solid solution of SrO in γ-Fe₂O₃. This solid solution phase behaves as an intermediate and undergoes further reaction with γ-Fe₂O₃ to give SrFe₁₂O₁₉. No paramagnetic Sr-Fe oxide intermediate is formed. The low temperature of the reactions and the absence of paramagnetic intermediates offer new possibilities for controlling the textures and magnetic properties SrFe₁₂O₁₉ ceramic bodies.

PACS numbers: 81.20.Lb, 75.50.Gg, 75.60.Gm, 76.80. + y

INTRODUCTION

Several investigators (1,2) have independently established that SrFeO_{3-x} is an intermediate in the formation of SrFe₁₂O₁₉ from mechanical mixtures of SrCO₃ and Fe₂O₃ in air via the consecutive reactions listed below:



Since reaction (1) does not occur at an appreciable rate until approximately 720 °C, the reported formation of the magnetoplumbite type hexaferrites of barium, strontium and lead at temperatures below 600 °C (3) suggests the possibility of other reaction mechanisms for the formation of SrFe₁₂O₁₉ in which SrFeO_{3-x} is not an intermediate. Because of the enhanced possibilities for controlling the chemical composition and textures afforded by lower formation temperatures when coprecipitated ferric hydroxide and strontium laurate are employed as starting materials, it is desirable to characterize the reaction mechanism as fully as possible. Therefore, we are reporting here the results of our investigation of the mechanism for the formation of SrFe₁₂O₁₉ from coprecipitated iron hydroxide and strontium laurate.

EXPERIMENTAL

Coprecipitates of Fe(OH)₃·nH₂O, ferric hydroxide, and Sr[CH₃(CH₂)₁₀COO]₂, strontium laurate, were prepared according to a previously published procedure (3) from iron nitrate, strontium nitrate, lauric acid and ammonium hydroxide, all of which were at least 99.5 per cent pure. In contrast to the earlier procedure, the coprecipitate was dried at 25 °C in a vacuum desiccator instead of at 900 °C in air. In addition, the decomposition of strontium laurate and further dehydration were also performed under vacuum at 300 °C. Decomposition of strontium laurate in air is accompanied by spontaneous combustion of the organic material, loss of temperature control and probably local heating to temperatures well above 300 °C and would have been detrimental to the aims of this study.

The starting materials and reaction products were characterized by powder x-ray diffraction, employing Ni-filtered CuK radiation, and scanning electron microscopy.

⁵⁷Fe Mössbauer spectroscopy was the principal tool for

following the course of the reaction, its sensitivity to the presence of small amounts of paramagnetic phases in mixtures with other magnetically ordered iron oxide phases having been demonstrated in earlier studies (2,4). All spectra were obtained at 298 K; the spectrometer and the data analysis techniques were similar to those described earlier (2,4). The isomer shifts are given relative to iron metal.

RESULTS AND DISCUSSION

The material resulting from firing the coprecipitated iron hydroxide and strontium laurate at 300 °C in vacuum exhibited an x-ray powder diffraction pattern in which ferric hydroxide was the major phase. Lines other than those appropriate to ferric hydroxide were present but could not be assigned definitively to SrO. By means of scanning electron microscopy it was established that no segregation of Sr and Fe existed for regions less than one micron in diameter. Due to the high agglomeration of the particles, details of particle morphology and the overall texture of the coprecipitates have not been established. At this stage in the reaction, the material exhibited no evidence for the development of a spontaneous magnetization. This result is consistent with the ⁵⁷Fe Mössbauer spectrum shown in Fig. 1. The spectrum is well-accounted for by assuming the presence of two quadrupole doublets with the following parameters: ΔE_Q(1) = 0.683 mm s⁻¹, δ(1) = 0.320 mm s⁻¹, and a relative area of 0.89; ΔE_Q(2) = 0.208 mm s⁻¹, δ(2) = 0.403 mm s⁻¹, and a relative area of 0.11. The parameters for doublet 1 are in good agreement with those previously reported for ferric hydroxide (5), confirming the x-ray powder diffraction measurements. The second doublet could be due to a second crystallographic species of iron in ferric hydroxide which was not detected in the earlier investigation (5) or it could be due to a phase containing both strontium and iron. None of the Mössbauer parameters are consistent with the presence of SrFeO_{3-x} (2,4).

Upon an increase in the firing temperature in air, evidence in the Mössbauer spectrum for a magnetically ordered phase is observed for a sample fired as low as 500 °C. The reaction rate, however, is extremely low. The spectrum for a sample fired in air at 550 °C for 600 secs is shown in Fig. 2. The ferric hydroxide has reacted fully to give a magnetically ordered phase, which from its response to a permanent magnet exhibits a large spontaneous moment. X-ray powder diffraction shows γ-Fe₂O₃ to be present; and fitting a single

magnetic hyperfine pattern to the spectrum resulted in the following parameters: $H_{\text{eff}} = 485 \text{ kOe}$, $\delta = 0.320 \text{ mm s}^{-1}$, $\Delta E_Q = 0.0 \text{ mm s}^{-1}$, and a width for lines 1 and 2 of 0.85 mm s^{-1} and 0.50 mm s^{-1} , respectively, which are consistent with those reported for $\gamma\text{-Fe}_2\text{O}_3$ (6) when the spectrum is fitted to a single magnetic hyperfine pattern. None of the iron oxyhydroxide (FeOOH) phases exhibits Mössbauer parameters similar to these at 298 K and can be eliminated from further consideration; the presence of these phases can also be ruled out on the basis of the spontaneous magnetization exhibited.

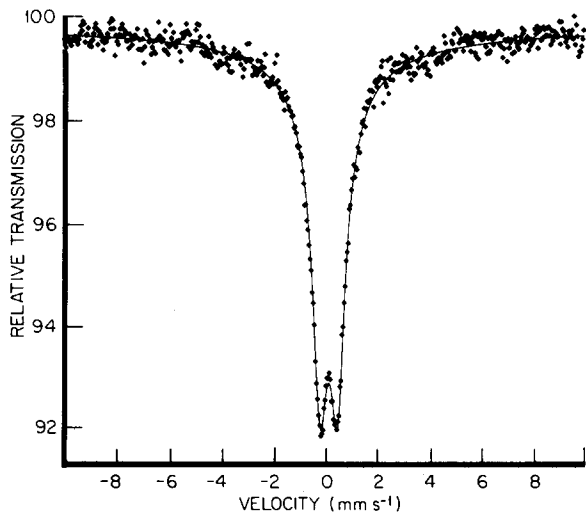


Fig. 1. ^{57}Fe Mössbauer spectrum at 298 K of strontium laurate/ferric hydroxide coprecipitate after heating in vacuum at 300°C for 10^5 secs. The solid line represents a fit of two quadrupole doublets.

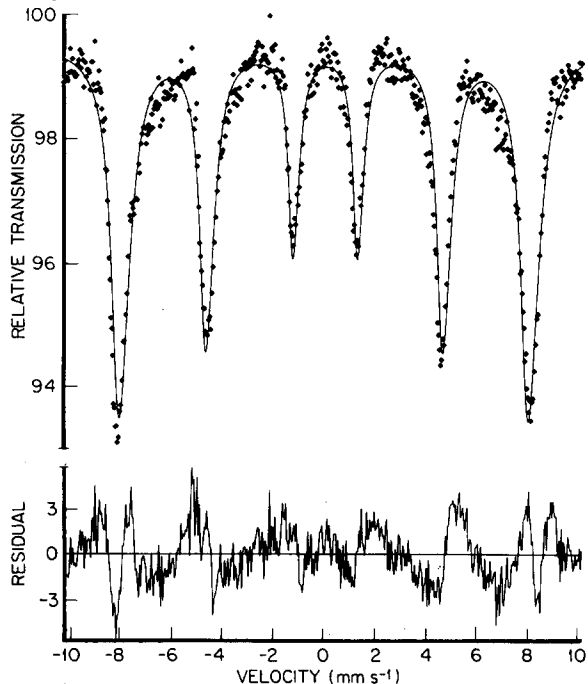


Fig. 2. ^{57}Fe Mössbauer spectrum at 298 K of the material whose spectrum is shown in Fig. 1 after firing at 550°C in air for 600 secs. The solid line through the data points is the result of fitting a single magnetic hyperfine pattern to the spectrum.

It is obvious from the plot of the residual in Fig. 2, that, due to spectral components unrelated to the two Fe sites in $\gamma\text{-Fe}_2\text{O}_3$ itself, a single magnetic pattern is inadequate to account for the spectrum. A fit of two magnetic hyperfine patterns resulted in two sets of parameters, one of which was nearly identical to those listed above for $\gamma\text{-Fe}_2\text{O}_3$ and one

with $H_{\text{eff}} = 450 \text{ kOe}$, $\delta = 0.28 \text{ mm s}^{-1}$ and a width for line 1 of 2.3 mm s^{-1} . The relative areas were 0.58 for the $\gamma\text{-Fe}_2\text{O}_3$ pattern and 0.42 for the pattern with the smaller H_{eff} and larger linewidths.

The spectrum of a sample heated for 6×10^4 secs at 550°C is shown in Figs. 3 and 4. The result of fitting a single magnetic pattern to the spectrum is displayed in Fig. 3 and a two magnetic pattern fit is displayed in Fig. 4. The inadequacy of the single pattern fit is more obvious in Fig. 3 than in Fig. 2 as a result of an increase in the relative area to 0.48 of the pattern with the lower H_{eff} and decrease in the width of line 1

to 1.7 mm s^{-1} . With the exception of these changes, the hyperfine parameters are quite similar to those observed for the sample fired for 600 secs at 550°C (Cf. Fig. 2). After firing the sample in air at 550°C for 6×10^5 secs, the spectrum in Fig. 5 is obtained. The more intense component is still to be associated, in part, with $\gamma\text{-Fe}_2\text{O}_3$ whose Mössbauer parameters are similar to those for the spectra in Figs. 2-4, except for a small increase in H_{eff} to 494 kOe and an apparent increase in relative area to 0.70. The less intense pattern exhibits lines with widths typical of ferrites, and the following hyperfine parameters: $H_{\text{eff}} = 412 \text{ kOe}$, $\delta = 0.37 \text{ mm s}^{-1}$ and

$\epsilon = 0.16 \text{ mm s}^{-1}$ (ϵ is the shift in the position of a single line in the spectrum due to the electric quadrupole interaction). These parameters are identical to those of the 12k site in $\text{SrFe}_{12}\text{O}_{19}$ (4). If the less intense pattern in Fig. 5 is due to Fe^{3+} on "12k-like" lattice sites, then the 2a, $4f_1$, and $4f_2$ sites of the magnetoplumbite structure would have patterns strongly overlapping that nominally assigned to $\gamma\text{-Fe}_2\text{O}_3$. If this be true, then the origin of the increase in H_{eff} of the nominal " $\gamma\text{-Fe}_2\text{O}_3$ pattern" is readily apparent. Assuming the same relative intensities for the 12k, $4f_1$, $4f_2$ and 2a sites in the material under consideration as in bulk $\text{SrFe}_{12}\text{O}_{19}$, the relative intensity of the pattern due only to $\gamma\text{-Fe}_2\text{O}_3$ is estimated to decrease to 0.38. This estimate is only of qualitative significance since the contribution of the intermediate phase is severely obscured as a result of its low intensity and strong overlap of the different patterns.

Upon further firing at 550°C in air for 6×10^6 secs, the spectrum appropriate to the fully formed $\text{SrFe}_{12}\text{O}_{19}$ is obtained as shown in Fig. 6.

CONCLUSIONS

The present investigation has confirmed the synthesis of $\text{SrFe}_{12}\text{O}_{19}$ at 550°C from coprecipitated ferric hydroxide and strontium laurate. The reaction rate at this temperature is still too low for practical applications; an extrapolation of the increase in reaction rate due to an increase in firing temperature from 500°C to 550°C indicates that well-crystallized $\text{SrFe}_{12}\text{O}_{19}$ could be obtained at 600°C as a result

of firing for a period of time on the order of 10^3 secs.

The reaction mechanism is quite different from that when SrCO_3 and $\gamma\text{-Fe}_2\text{O}_3$ are used as reactants. It is noteworthy that the iron oxide phase is $\gamma\text{-Fe}_2\text{O}_3$ which contains some of the structural elements required for the formation of $\text{SrFe}_{12}\text{O}_{19}$. The intermediate phase in this case appears to be strontium substituted $\gamma\text{-Fe}_2\text{O}_3$ which is identified with the component in the Mössbauer spectrum having the

lower H_{eff} and large linewidths. The initial increase in the intensity and decrease in linewidth occasioned by increasing the firing time from 600×10^4 secs are consistent with this component being due to an intermediate phase. Between a firing time of 6×10^5 secs, this intermediate phase is transformed into an incipient hexaferrite in which the lattice

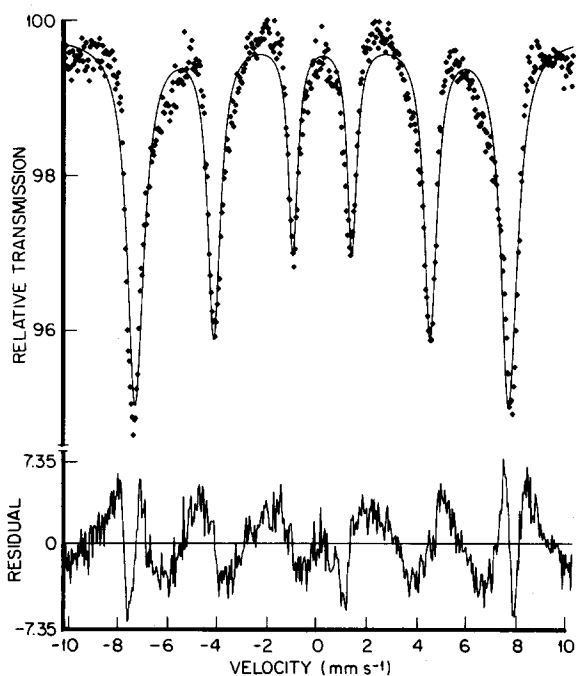


Fig. 3. ^{57}Fe Mössbauer spectrum at 298 K of the reaction mixture of Fig. 1 after firing in air at 550°C for 6×10^4 secs. The solid line represents a fit of one magnetic hyperfine patterns.

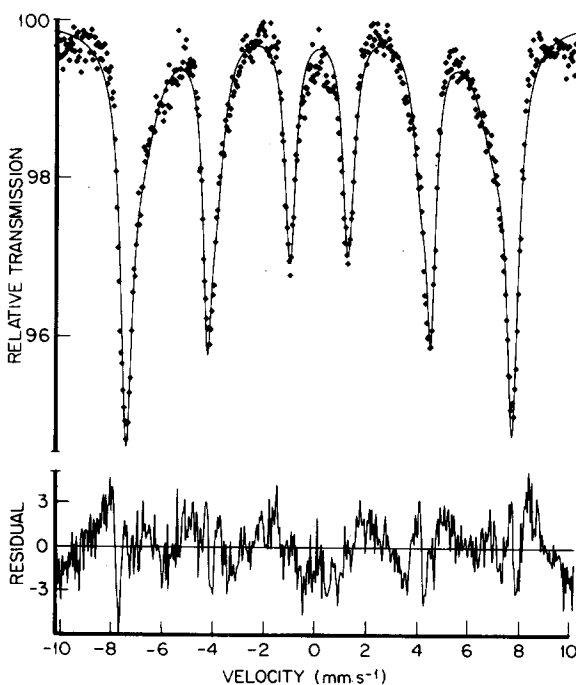


Fig. 4. Same as in Fig. 3, except for a fit of two magnetic hyperfine patterns.

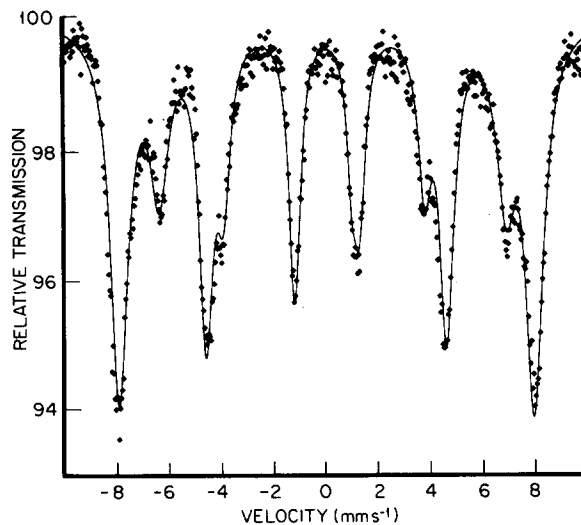


Fig. 5. ^{57}Fe Mössbauer spectrum at 298 K of the reaction mixture of Fig. 1 after firing in air at 550°C for 6×10^5 secs along with a two pattern fit.

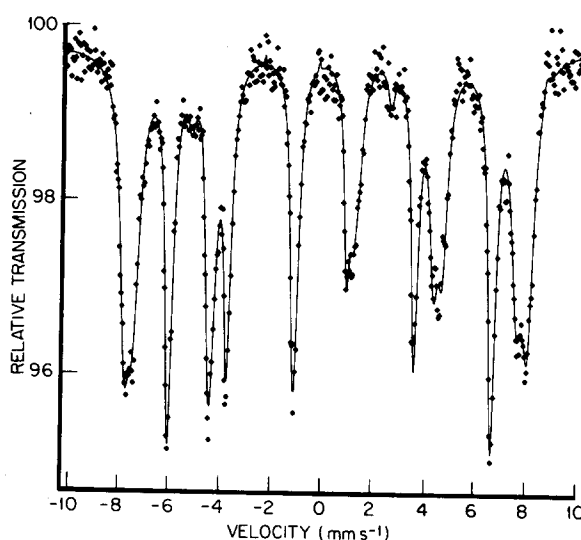


Fig. 6. 298 K ^{57}Fe Mössbauer spectrum of the reaction mixture of Fig. 1 after firing at 550°C in air for 6×10^6 secs, demonstrating the formation of $\text{SrFe}_{12}\text{O}_{19}$.

of 12k sites is highly developed. This result provides further evidence for the proposed reaction mechanism since the 12k sites are on the boundary between the spinel and R blocks in the magnetoplumbite structure.

REFERENCES

- a) Supported in part by a NATO Grant.
- 1) Haberey, F. and Kockel, A., IEEE Trans. Mag. MAG 12, 983 (1976).
- 2) Vogel, R. and Evans, B. J., J. de Phys. C2 277 (1979).
- 3) Micheli, A. L., U. S. Pat. 3,634,254, 1972.
- 4) Vogel, R. H. and Evans, B. J., J. Magn. Mag. Mat. 13, 294 (1979).
- 5) Srivastava, B. N. and Singh, R. P., Indian J. P. Appl. Phys. 12, 311 (1974).
- 6) Evans, B. J., Ph.D. Thesis, U. Chicago, 1968.