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SOLID STATE- AND MAGNETO-CHEMISTRY OF THE SrO-Fe_2O_3 SYSTEM

III. The non-existence of single-phase "$SrFe_2O_4$"

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A detailed Mössbauer investigation of 1 : 1 SrO : Fe_2O_3 has shown that a single phase with the $SrFe_2O_4$ composition does not exist in the SrO–Fe_2O_3 system when $SrCO_3$ and Fe_2O_3 are reacted in air. A multiphase assemblage of $SrFe_{12}O_{19}$, $Sr_4Fe_6O_{13}$, and $SrFeO_{3-x}$ is observed in the material with an overall composition of "$SrFe_2O_4$". By means of novel analyses of the complex Mössbauer spectra of the 1 : 1 SrO : Fe_2O_3 composition, all of the Fe containing phases have been identified and their respective mole percentages determined. The relative amounts of the phases present depend on the final firing temperature. The published X-ray powder data for "$SrFe_2O_4$" can be interpreted satisfactorily in terms of the Mössbauer results, i.e., as a multiphase assemblage, and corresponds to a low temperature assemblage of $SrFe_{12}O_{19}$, $Sr_4Fe_6O_{13}$ and $SrFeO_{3-x}$ for the overall composition of "$SrFe_2O_4$.

1. Introduction

$SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ are isomorphous hexagonal ferrites with the magnetoplumbite structure, and both compounds can be synthesized by high temperature, solid state reactions of the appropriate carbonate with Fe_2O_3. In the case of $BaFe_{12}O_{19}$, $BaCO_3$ reacts with Fe_2O_3 at 1048 K to form the monoferrite $BaFe_2O_4$. This intermediate phase then reacts with the remaining Fe_2O_3 above 1173 K to form the magnetoplumbite-type hexagonal ferrite [1]. This reaction has been extensively investigated [2]. In contrast, few detailed investigations of the mechanism responsible for the formation of $SrFe_{12}O_{19}$ have been reported [3,4] and even in these cases the results have been contradictory. One of the discrepancies among the results of these investigations centers around the question of whether or not $SrFe_2O_4$ exists as a single phase. Berekta and Brown [3] reported the presence of $SrFe_2O_4$ as an intermediate phase during the formation of $SrFe_{12}O_{19}$ in air, and also reported the presence of the $SrFe_2O_4$ phase in a 4 : 3 mixture of SrO : Fe_2O_3. These authors question the assignment of the $SrFe_2O_4$ phase to the hexagonal system [5], and suggest an assignment to the orthorhombic system based on a study of $CaFe_2O_4$ by Hill et al. [6]. However, evidence for the existence of $SrFe_2O_4$ and its characterization are inadequate.

More recently, Haberey and Kockel [4] reported the oxygen deficient perovskite $SrFeO_{3-x}$ as the only iron containing intermediate phase involved in the formation of $SrFe_{12}O_{19}$ from $SrCO_3$ and Fe_2O_3 in air, and were unable to synthesize a single phase material with the $SrFe_2O_4$ composition. It has subsequently been established that $SrFeO_{3-x}$ is the principal intermediate phase in the formation of $SrFe_{12}O_{19}$ from $SrCO_3$ and Fe_2O_3 in air [7]. These latter experiments [7] raised further concerns with regards to the existence of $SrFe_2O_4$ and any role this phase might play in the formation of $SrFe_{12}O_{19}$.

These questions concerning $SrFe_2O_4$ are important to an understanding of the magnetic properties of $SrFe_{12}O_{19}$ since appreciable variations in the magnetic properties result from only minor variations in the SrO : Fe_2O_3 stoichiometry, i.e., 1 : 6 to 1 : 5, and in the heat treatment schedule. Superior magnetic properties are obtained for a 1 : 5.5 composition [8]. Since it has been shown [7] that the Mössbauer parameters are very similar for the 1 : 6, 1 : 5.5 and 1 : 5 compositions, the excess strontium probably exists in the form

of an additional strontium rich phase (or phases) whose spectrum is not resolved from that of the 1 : 6 phase.

Both $SrFe_2O_4$ [9] and a phase with a composition that has been reported variously as $Sr_7Fe_{10}O_{12}$ and $Sr_4Fe_6O_{13}$ [7,10] have been suggested as candidates for the Sr-rich phase in the non-stoichiometric hexaferrite. Although the 4 : 3 phase is observed in a non-stoichiometric hexaferrite with a SrO : Fe_2O_3 ratio of 1 : 3 [7], the possibility that other phases, such as $SrFe_2O_4$, are also present cannot be ruled out. Therefore, an investigation of the $SrFe_2O_4$ composition would improve our understanding of the complex crystal chemical and physical interactions that lead to superior magnetic properties for the non-stoichiometric hexaferrites.

2. Experimental

Johnson Matthey Puratronix grade $SrCO_3$ and Fe_2O_3 were intimately mixed with an agate mortar and pestle to give three grams of the 1 : 1 SrO : Fe_2O_3 composition. The mixture was pressed into a pellet and calcined at 1008 K for four hours and reground. The majority of the sample was then subject to the heat treatment indicated in table 1.

X-ray powder diffraction patterns were obtained using a Guinier camera and Cu radiation. Mössbauer spectra were obtained using a constant acceleration, electromechanical spectrometer in conjunction with a 512 channel MCA. The spectra were computer analyzed by means of a least-mean-squares fitting program. This program contained all of the parameters needed to generate the Mössbauer spectra for the following phases: Fe_2O_3, $SrFe_{12}O_{19}$, $Sr_4Fe_6O_{13}$ and $Sr_2Fe_2O_5$. The program fitted the experimental data by varying the integrated intensities of each phase while keeping all other parameters constant. The paramagnetic phase $SrFeO_{3-x}$ was also fitted, but the Mössbauer parameters for this phase were not held constant during the fitting since they are known to be dependent on the oxygen partial pressure and the firing temperature [11]. Instead, the spectrum of the $SrFeO_{3-x}$ phase was fitted with three independent lines with all parameters variable.

In order to minimize differences between spectra due to extrinsic experimental effects, i.e., small non-linearities in the electronics and drive system, cosine broadening effects, impurities in the starting materials, etc., $SrFeO_{3-x}$, $Sr_4Fe_6O_{13}$, $Sr_2Fe_2O_5$ and $SrFe_{12}O_{19}$

Table 1
Sample firing and annealing schedules

Sample number	Initial firing	Intermediate firing	Final firing
1	1073 K – 12 h		
1a	1073 K – 12 h	1073 K – 48 h	
1b	1073 K – 12 h	1073 K – 48 h	1138 K – 48 h
2	1073 K – 12 h	1273 K – 24 h	
2a	1073 K – 12 h	1273 K – 24 h	1273 K – 48 h
3	1073 K – 12 h	1273 K – 24 h	1438 K – 48 h
4	1136 K – 96 h		
4a	1136 K – 96 h	1193 K – 48 h	

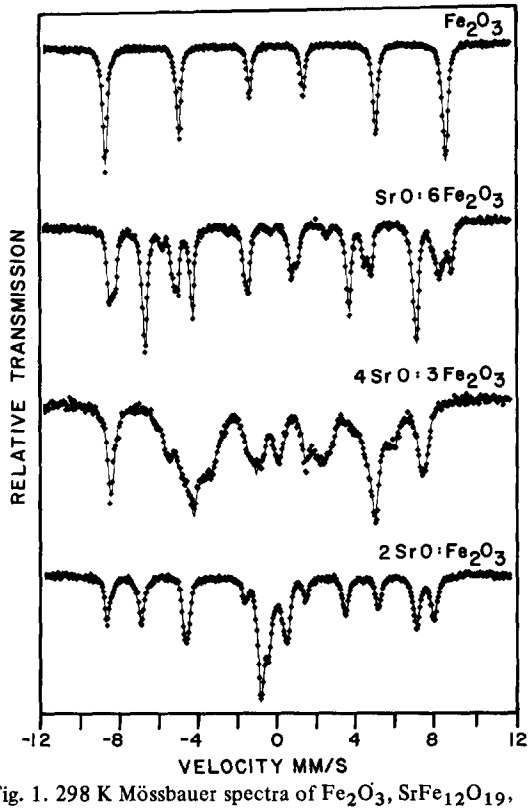

Fig. 1. 298 K Mössbauer spectra of Fe_2O_3, $SrFe_{12}O_{19}$, $Sr_4Fe_6O_{13}$, $Sr_2Fe_2O_5$, $SrFeO_{3-x}$. The Mössbauer parameters obtained from these spectra were used to fit the spectra of the 1 : 1 compositions. The spectra of the 2 : 1 composition shown here is a combination of the magnetically ordered $Sr_2Fe_2O_5$ and the paramagnetic $SrFeO_{3-x}$ phases.

were synthesized using the same starting materials as for the 1 : 1 SrO : Fe_2O_3 composition, and their spectra obtained on the same spectrometer system with source–absorber–detector geometry, velocity settings, and other instrumental factors held constant. Fig. 1 shows the spectra of the pure compositions synthesized in this study. The parameters obtained from the computer fitting of these spectra are shown in table 2 and were used to generate the spectra employed in fitting the spectra of the 1 : 1 Sr : Fe_2O_3 samples.

An alternative approach to fitting the spectra of the 1 : 1 composition would have been to release the constraints on the parameters of the pure compositions and minimize χ^2 with respect to all of the parameters instead of just the intensity parameter. However, this approach is unsatisfactory for a number of reasons. With the exception of the Fe_2O_3 and $SrFeO_{3-x}$ phases, the Mössbauer spectra for the pure strontium ferrite phases are very complex. The 1 : 6 phase has, for example, five Fe sites which lead to five, partially-resolved magnetic hyperfine patterns in the Mössbauer spectrum. Although little is known about the crystal structure of the 4 : 3 phase and therefore the number of Fe sites, the Mössbauer spectrum of this phase cannot be adequately fit with less than four (poorly resolved) magnetic hyperfine patterns. In addition to the poor resolution of the different components within the spectra of the single phase materials, there is considerable overlap between different components from the different phases. Thus there can be considerable swapping of intensity between different lines from different phases that would have little or no effect on the magnitude of χ^2 for an unconstrained fit but the intensities, themselves, would be without physical significance.

Such effects were observed, for example, when the spectrum of sample no. 1a was fit with freely variable parameters for the 1 : 6 SrO : Fe_2O_3 and Fe_2O_3 phases. Although the fitted values of H_{eff}, E_Q, IS for these two phases did not differ significantly from the

Table 2
Mössbauer parameters stored in fitting program. The isomer shifts are reported with respect to iron metal. Areas are calculated from normalized intensities

	$SrFe_{12}O_{19}$	$Sr_4Fe_6O_{13}$	$Sr_2Fe_2O_5$	Fe_2O_3
H_{eff} [a]	520	420	503	518
E_Q [b]	0.217	−0.333	0.303	−0.045
IS [b]	0.249	0.256	0.266	0.252
Area	0.462	1.20	1.07	1.19
H_{eff}	512	416	423	
E_Q	0.013	−0.318	0.223	
IS	0.225	0.099	0.030	
Area	0.147	1.13	1.22	
H_{eff}	494	303		
E_Q	0.147	0.339		
IS	0.125	0.098		
Area	0.488	0.843		
H_{eff}	414	253		
E_Q	0.236	0.292		
IS	0.191	0.055		
Area	1.20	4.23		
H_{eff}	412			
E_Q	1.17			
IS	0.134			
Area	0.131			

[a] AU H_{eff} values are in units of kOe.
[b] In units of mm s^{-1}.

values shown in table 2, the areas of some of the individual hyperfine patterns deviated widely from the expected ones. For example, the areas of the Fe_2O_3 pattern and the 2b site pattern of the 1 : 6 phase decreased nearly to zero and the areas of the $4f_2$ and 2a sites increased to unrealistically high proportions. The unconstrained fit gave a value of 0.013 ± 0.002 for the goodness of fit parameter Misfit [12] indicating a good fit to the data. On the other hand, the constrained fit achieved a Misfit value of 0.015 ± 0.002. This indicates the constrained model accurately accounts for all of the structure observed in the spectra while maintaining physically meaningful parameters and is therefore the more acceptable approach to use for the analysis of these complex spectra on both theoretical and practical grounds.

3. Results and discussion

The relative areas of each phase obtained from the Mössbauer spectra were used to calculate the mole percentages given in table 3. This procedure assumes that the recoilless fractions of the different iron sites are equal and that the intensity of the pattern is proportional to the amount of that phase present, i.e., the thin-absorber limit. In this approximation, the mole percent (m) of each phase i is given by the following expression:

$$m_i = 100[(A_i/n_i)/A_t] \,, \qquad (1)$$

where A_i is the integrated intensity of phase i, n_i is the number of Fe atoms per mole of phase i, and A_t is the sum of (A/n) for all phases present. To test the practical application of this relationship, the Mössbauer

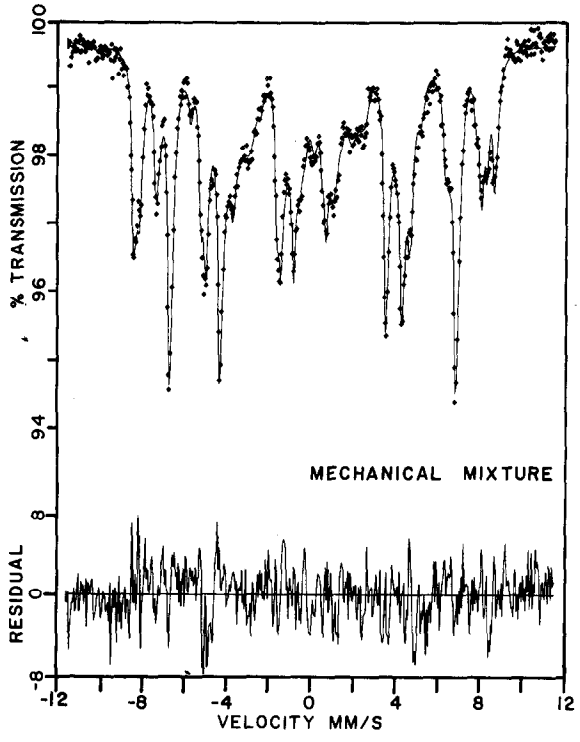

Fig. 2. 298 K Mössbauer spectra of a mechanical mixture of 31.7 mol% $SrFe_{12}O_{19}$, 51.2 mol% $Sr_4Fe_6O_{13}$ and 17.1 mol% $SrFeO_{3-x}$.

spectrum (fig. 2) of a mechanical mixture of 31.7 mol% $SrFe_{12}O_{19}$, 51.2 mol% $Sr_4Fe_6O_{13}$ and 17.1 mol% $SrFeO_{3-x}$ was fitted. Evaluation of the mole fractions of the separate phases using eq. (1) gave the following results: 31.8 mol% $SrFe_{12}O_{19}$, 50.5 mol% $Sr_4Fe_6O_{19}$ and 17.7 mol% $SrFeO_{3-x}$, in good agreement with the known mole fractions.

Table 3 lists the mole percentages of each phase

Table 3
Mössbauer determinations of the mole percentages of the phases present in the 1 : 1 SrO : Fe_2O_3 samples synthesized for this study

Phase	Sample number							
	1	1a	1b	4	4a	2	2a	3
Fe_2O_3	46.5	14.4	0	0	0	0	0	0
$SrFe_{12}O_{19}$	7.7	11.6	14.5	15.4	17.3	16.9	17.3	17.8
$Sr_4Fe_6O_{13}$	0	0	37.6	32.9	59.0	69.0	72.1	70.8
$SrFeO_{3-x}$	45.8	74.0	47.9	51.7	23.7	14.1	10.6	11.4

observed in the eight samples listed in table 1. The only iron containing phases observed in these samples were $SrFe_{12}O_{19}$, $Sr_4Fe_6O_{13}$, Fe_2O_3 and $SrFeO_{3-x}$. The $Sr_2Fe_2O_5$ phase was not observed in the Mössbauer spectra of these samples. The data indicate that lengthy firing times are necessary to achieve an equilibrium mixture of phases at the lower temperatures. There is a substantial change with time in the relative amounts of the three phases observed in the spectra of samples no. 1 and no. 1a; sample no. 1a is believed to closely approximate the equilibrium phase assemblage for 1073 K. At 1273 K, little change is observed in the phase composition between the initial firing and the subsequent annealing, indicating a rapid approach to equilibrium at this temperature. In addition, only small changes are observed in the relative amounts of the phases present within the temperature range 1273 to 1483 K (sample no. 2–no. 3). Below 1273 K the phases present and their relative amounts show a strong dependence on the firing time; however, the similar compositions of sample no. 1b and no. 4 which underwent final equilibration at approximately the same temperature, but had different thermal histories, indicate that the phase assemblage for this overall phase analyses is primarily a function only of the final firing temperature and there is not evidence for the presence of metastable phases.

The Mössbauer spectra for samples no. 1a, no. 1b, no. 4a and no. 3, respectively, are shown in figs. 3 and 4. The strong paramagnetic component in the spectrum of sample no. 1a is due to the $SrFeO_{3-x}$ phase. The 4 : 3 phase is evident in the spectrum of sample no. 1b, increases in intensity in sample no. 4a and has become the dominant phase in the spectrum of sample no. 3.

The X-ray powder diffraction data of samples no. 2 through no. 4a are not identical to that reported for

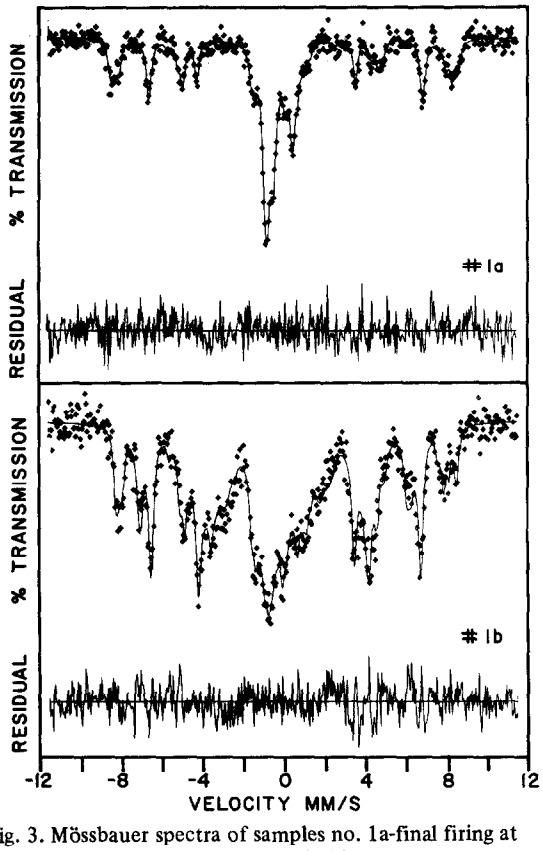

Fig. 3. Mössbauer spectra of samples no. 1a-final firing at 1073 K, and no. 1b-final firing at 1138 K.

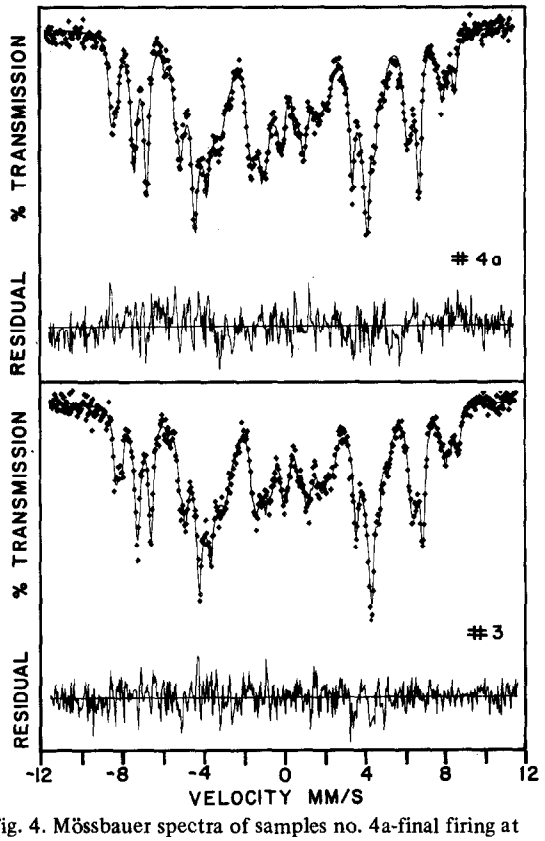

Fig. 4. Mössbauer spectra of samples no. 4a-final firing at 1193 K, and no. 3-final firing at 1438 K.

Table 4
Comparison of the X-ray data for the sample no. 1a with previously reported data for Sr-Fe-O phases, including "$SrFe_2O_4$"

$SrFe_2O_4$ ASTM 1-1027		SrO : Fe_2O_3 this work		$SrFeO_{3-x}$ ref. [4]		$SrFe_{12}O_{19}$ ASTM 24-1207		Fe_2O_3 ASTM 13-534	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
		4.33	w	3.86	3				
3.08	6					3.07	2		
2.93	2	2.951	w			2.94	32		
		2.865	vw			2.88	17		
		2.773	w			2.77	90		
2.75	100	2.750	vs	2.75	100				
		2.707	w					2.69	100
2.61	10	2.629	mw			2.62	100		
2.52	8	2.530	vw			2.53	8	2.51	50
2.41	8	2.426	vw			2.42	51		
2.24	10	2.235	mw	2.25	11	2.23	45		
1.95	30	1.941	m	1.95	34	1.94	5		
1.90	4								
1.66	2	1.663	vw			1.66	50	1.69	60
1.62	4	1.620	vw			1.63	32		
1.59	40	1.581	m	1.59	33	1.60	11		
1.47	4	1.471	vw			1.47	80		
1.37	20	1.370	mw	1.38	18				
1.23	16	1.225	w	1.23	12				
1.12	2	1.1074	vw	1.12	5				
1.04	12	1.0372	mw	1.04	14				

"$SrFe_2O_4$"; however, the data are consistent with the Mössbauer results, i.e., all of the observed reflections can be assigned to one of the three phases identified in the Mössbauer spectra of these samples. The X-ray diffraction data for sample no. 1a agree quite well with that reported for a material with the overall composition "$SrFe_2O_4$" [5]. Table 4 shows the correlation between the X-ray data for sample no. 1a and the ASTM card for "$SrFe_2O_4$" as well as the assignment of the reflections to the three phases identified in the Mössbauer spectrum of sample no. 1a. The line with a d spacing of 3.08 Å was not observed in our diffraction pattern, but it can be assigned to the 1 : 6 phase. The difference in intensities of the diffraction lines is probably due to texture effects. The 1.90 Å reflection reported in the ASTM card of "$SrFe_2O_4$" (table 4) can be assigned to the 4 : 3 phase. Although the 1.90 Å line of the 4 : 3 phase is not the strongest reflection observed for this phase, it is the only moderately strong line that is not overlapped by lines from the 1 : 6 or $SrFeO_{3-x}$ phases. The strongest lines of the 4 : 3 phase (2.79 Å, 2.78 Å, 2.73 Å) lie very close to the very strong 2.75 Å line from the $SrFeO_{3-x}$ phase and the strong reflection of 2.77 Å from the 1 : 6 composition. Consequently, it is difficult to resolve the individual lines at approximately 2.75 Å. The 1.90 Å reflection does appear in the samples fired above 1073 K, which is in agreement with the increasing concentration of $Sr_4Fe_6O_{13}$ with increasing temperature (cf. table 3).

4. Conclusions

The results of the present study definitely establish that a $SrFe_2O_4$ single phase material does not result from the high temperature solid state reaction between $SrCO_3$ and Fe_2O_3 in air. The 1 : 1 composition is a multi-phase assemblage of $SrFeO_{3-x}$, $SrFe_{12}O_{19}$ and $Sr_4Fe_6O_{13}$. The previously published X-ray data for "$SrFe_2O_4$" agree with the Mössbauer and X-ray results of this study and would correspond to a low temperature phase assemblage on the basis of the present investigation. $SrFeO_{3-x}$ is the most abundant phase

at temperatures below 1150 K. At 1193 K, the 4 : 3 composition becomes the dominant phase; however, both $SrFe_{12}O_{19}$ and $SrFeO_{3-x}$ are still present. This result is contrary to the phase diagram of Batti [10] in which only the 1 : 6 and 4 : 3 (7 : 5) phases are shown to coexist for the 1 : 1 composition at 1438 K.

The stable three phase field observed in this study indicates that the $SrO-Fe_2O_3$ system cannot be treated as a binary system in the presence of free oxygen; rather, the ternary system $SrO-Fe_2O_3-O_2$ is more appropriate under these conditions. The presence of both the 1 : 6 and 4 : 3 phase in the 1 : 1 composition makes it highly probable that the 4 : 3 phase is also present in a 1 : 5.5 $SrO : Fe_2O_3$ composition as suggested previously. Although this study shows that $SrFeO_{3-x}$ is stable in the presence of $Sr_4Fe_6O_{13}$ and $SrFe_{12}O_{19}$ in the 1 : 1 $SrO : Fe_2O_3$ composition, we have no evidence that $SrFeO_{3-x}$ is also present in the 1 : 5.5 composition. Nevertheless, the $Sr_4Fe_6O_{13} : SrFeO_{3-x}$ ratio of 6 : 1 observed in the 1 : 1 composition above 1273 K suggests the amount of $SrFeO_{3-x}$ present in the 1 : 5.5 composition would be negligible, if present at all.

Even though we believe the questions and controversies regarding the existence of the material with the $SrO : Fe_2O_3$ overall composition have been resolved, the true complexity of the $SrO-Fe_2O_3$ system has also been revealed to be greater than previously surmised. A common pitfall which has plagued many investigations of the $SrO-Fe_2O_3$ system has been the tendency of the investigator to draw analogies between the $SrO-Fe_2O_3$ system and the $BaO-Fe_2O_3$ system. The present investigation has shown that not only does the $SrO-Fe_2O_3$ system behave differently from the $BaO-Fe_2O_3$ system, but that conventional analysis of X-ray and Mössbauer data can lead to erroneous conclusions concerning the $SrO-Fe_2O_3$ system. Further work under controlled atmospheres is necessary in order to develop even a moderately complete understanding of the solid state reactions and phase assemblages in the $SrO-Fe_2O_3-O_2$ system. We believe that the analytical techniques developed for the present investigation will also prove useful in these future studies.

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