PHASE FORMATION AND STRUCTURAL TRANSFORMATION OF STRONTIUM FERRITE SrFeO$_x$

BY

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Declaration

This thesis does not incorporate any material previously submitted for a degree, or diploma at any university and to the best of my knowledge and belief, does not contain any material previously published or written by another person except where due reference is made in the text.

Marek W. Schmidt
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Abstract

Non-stoichiometric strontium iron oxide is described by an abbreviated formula \( \text{SrFeO}_x \) \((2.5 \leq x \leq 3.0)\) exhibits a variety of interesting physical and chemical properties over a broad range of temperatures and in different gaseous environments. The oxide contains a mixture of iron in the trivalent and the rare tetravalent state. The material at elevated temperature is a mixed oxygen conductor and it, or its derivatives, can have practical applications in oxygen conducting devices such as pressure driven oxygen generators, partial oxidation reactors in electrodes for solid oxide fuel cells (SOFC).

This thesis examines the behaviour of the material at ambient and elevated temperatures using a broad spectrum of solid state experimental techniques such as: x-ray and neutron powder diffraction, thermogravimetric and calorimetric methods, scanning electron microscopy and Mössbauer spectroscopy. Changes in the oxide were induced using conventional thermal treatment in various atmospheres as well as mechanical energy (ball milling).

The first experimental chapter examines the formation of the ferrite from a mixture of reactants. It describes the chemical reactions and phase transitions that lead to the formation of the oxide. Ball milling of the reactants prior to annealing was found to eliminate transient phases from the reaction route and to increase the kinetics of the reaction at lower temperatures. Examination of the thermodynamics of iron oxide (hematite) used for the reactions led to a new route of synthesis of the ferrite from magnetite and strontium carbonate. This chapter also explores the possibility of synthesis of the material at room temperature using ball milling.

The ferrite strongly interacts with the gas phase so its behaviour was studied under different pressures of oxygen and in carbon dioxide. The changes in ferrite composition have an equilibrium character and depend on temperature and oxygen concentration in the atmosphere. Variations of the oxygen content \( x \) were described as a function of temperature and oxygen partial
pressure, the results were used to plot an equilibrium composition diagram. The heat of oxidation was also measured as a function of temperature and oxygen partial pressure.

Interaction of the ferrite with carbon dioxide below a critical temperature causes decomposition of the material to strontium carbonate and SrFe\(_{12}\)O\(_{19}\). The critical temperature depends on the partial pressure of CO\(_2\) and above the critical temperature the carbonate and SrFe\(_{12}\)O\(_{19}\) are converted back into the ferrite. The resulting SrFe\(_{12}\)O\(_{19}\) is very resistant towards carbonation and the thermal carbonation reaction does not lead to a complete decomposition of SrFeO\(_x\) to hematite and strontium carbonate.

The thermally induced oxidation and carbonation reactions cease at room temperature due to sluggish kinetics however, they can be carried out at ambient temperature using ball milling. The reaction routes for these processes are different from the thermal routes. The mechanical oxidation induces two or more concurrent reactions which lead to samples containing two or more phases. The mechanical carbonation on the other hand produces an unknown metastable iron carbonate and leads a complete decomposition of the ferrite to strontium carbonate and hematite.

Thermally and mechanically oxidized samples were studied using Mössbauer spectroscopy. The author proposes a new interpretation of the Sr\(_4\)Fe\(_4\)O\(_{11}\) (\(x = 2.75\)) and Sr\(_8\)Fe\(_8\)O\(_{23}\) (\(x = 2.875\)) spectra. The interpretation is based on the chemistry of the compounds and provides a simpler explanation of the observed absorption lines. The Mössbauer results from a range of compositions revealed the room temperature phase behaviour of the ferrite also examined using x-ray diffraction.

The high-temperature crystal structure of the ferrite was examined using neutron powder diffraction. The measurements were done at temperatures up to 1273 K in argon and air atmospheres. The former atmosphere protects Sr\(_2\)Fe\(_2\)O\(_5\) (\(x = 2.5\)) against oxidation and the measurements in air allowed variation of the composition of the oxide in the range 2.56 ≤ \(x\) ≤ 2.81. Sr\(_2\)Fe\(_2\)O\(_5\) is an antiferromagnet and undergoes phase transitions to the paramagnetic state at 692 K and from the orthorhombic to the cubic structure around 1140 K. The oxidized form of the ferrite also undergoes a transition to the high-temperature cubic form. The author proposes a new structural model for the cubic phase based on a unit cell with the \(Fm\bar{3}c\) symmetry. The new model allows a description of the high-temperature cubic form of the ferrite as a solid solution of the composition end members. The results
were used to draw a phase diagram for the SrFeO$_x$ system.

The last chapter summarizes the findings and suggests directions for further research.
This addendum contains explanations to points raised by examiners.

1. **Question concerning x-ray diffraction lines intensity ratio I(150)/I(161) used to assess iron contamination in section 3.5.1 of the thesis.**

   An intensity ratio of 0.45 for the Fe/Sr=1.01 composition was observed from the x-ray diffraction pattern. Experiments were also conducted on several other samples with different Fe/Sr ratios. In all cases, increasing iron fraction caused an increase in the I(150)/I(161) ratio. Only samples with compositions Fe/Sr=1.01 and 1.05 were shown in the thesis for the sake of brevity to demonstrate the detection threshold. The detection method was designed to screen milled samples and discard those contaminated with iron, not to quantify the contamination level.

   SEM examination of Sr$_2$Fe$_2$O$_5$ powders has shown that Sr$_2$Fe$_2$O$_5$ microcrystals do not develop facets (see Figure 4.17). As a result, the crystals cannot align during x-ray specimen preparation and cause substantial preferred orientation. The fraction of Sr$_4$Fe$_6$O$_{13}$ phase was small and the much larger amount of Sr$_2$Fe$_2$O$_5$ should diminish potential orientation of Sr$_4$Fe$_6$O$_{13}$ crystals, which should be randomly oriented within Sr$_2$Fe$_2$O$_5$ grains.

2. **Question concerning section 3.5.2 of the thesis.**

   During the experimental work the author prepared a variety of Sr-Fe-O samples with compositions in the range 1<Fe/Sr<12 in order to confirm the phase behaviour of the Sr-Fe-O system found in the literature. These experiments were needed to investigate the transient phases occurring during synthesis of SrFeO$_x$ (see section 3.2). Special emphasis was placed on composition ranges around Fe/Sr=1.43 (Sr$_7$Fe$_{10}$O$_{22}$) and Fe/Sr=2 (SrFe$_2$O$_4$). The samples were examined using x-ray diffraction and simple phase identification, based on the diffraction lines, showed that, for these compositions, the Sr-Fe-O system forms only mixtures of two phases, not a single phase as claimed in the cited literature. The lack of the SrFe$_2$O$_4$ phase was also confirmed by the work of Vogel and Evans [A] found after submission of the thesis.

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1 The references marked with numerals refer to the bibliography section of the thesis. References marked with letters are additional and are collected at the end of the addendum.

Indexing of the synchrotron diffraction patterns of Sr\textsubscript{4}Fe\textsubscript{4}O\textsubscript{11} and Sr\textsubscript{8}Fe\textsubscript{8}O\textsubscript{23} yielded ambiguous results, pointing at two or three different crystal structures. The goodness-of-fit obtained during the indexing procedure was similar for all models, making it impossible to choose one structure. Rietveld refinement was not carried out since the internal structures of Sr\textsubscript{4}Fe\textsubscript{4}O\textsubscript{11} and Sr\textsubscript{8}Fe\textsubscript{8}O\textsubscript{23} are unknown and a multiple-parameter fit could lead to a wrong solution, despite a good fit (see remarks on the Rietveld method in section 2.3.1).

The use of high-resolution neutron diffraction to study Sr\textsubscript{4}Fe\textsubscript{4}O\textsubscript{11} and Sr\textsubscript{8}Fe\textsubscript{8}O\textsubscript{23} may have its advantages because of a different scattering mechanism that would enhance structural features associated with oxygen.

4. Questions concerning the choice of symmetry group (Fm\textsubscript{3}c over Pm\textsubscript{3}m).

The problem of the symmetry group of high-temperature cubic SrFeO\textsubscript{x} (x<3) was addressed because of discrepancies in the literature. Shin et al. [159] proposed a perovskite cell for cubic Sr\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} but later noticed that the cell contains only half the atoms within the oxide molecule (Z=0.5) [165]. The unit cell proposed in the thesis (Fm\textsubscript{3}c) does not overturn completely the previous findings but was constructed to incorporate the chemical makeup of the ferrite.

Atoms building the SrFeO\textsubscript{x} structure are charged when engaged in forming of a chemical compound. The unit cell is usually chosen to contain at least one chemical molecule, as illustrated in publications dealing with room temperature phases Sr\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5}, Sr\textsubscript{4}Fe\textsubscript{4}O\textsubscript{11} and Sr\textsubscript{8}Fe\textsubscript{8}O\textsubscript{23}: the proposed unit cells always contain whole numbers of molecules as depicted by chemical formulae not their fractions [138,139,160,161]. In the case of high-temperature cubic phases, authors tend to use the abbreviated notation SrFeO\textsubscript{2.5}, SrFeO\textsubscript{2.75} and SrFeO\textsubscript{2.875} to justify the perovskite model [127,128]. However, the only aspect that changes upon the transition to the cubic form is the arrangement of atoms not the chemical makeup. So, the correct chemical formulae of the high-temperature phases are still Sr\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5}, Sr\textsubscript{4}Fe\textsubscript{4}O\textsubscript{11} and Sr\textsubscript{8}Fe\textsubscript{8}O\textsubscript{23}.

The analysis of cubic SrFeO\textsubscript{x} was based on the results of the neutron powder diffraction experiments. The analysis began with the Sr\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} phase and was then extended to the other oxygen deficient phases Sr\textsubscript{4}Fe\textsubscript{4}O\textsubscript{11} and Sr\textsubscript{8}Fe\textsubscript{8}O\textsubscript{23}. Cubic neutron diffraction patterns were indexed and the simplest solution gave the small "perovskite" cell with a lattice constant of about 3.9Å. At this stage no assumption
was made as to the atomic layout inside the cell. Since the volume of the cell and the chemical formula of the compound were known, the next step was to assess the number of oxide molecules in the cell. This is a standard procedure in crystal structure determination [56,B]. The number of molecules per cell, Z, the density of crystal ρ, the molecular weight M of the molecule and the volume of the unit cell, V, must fulfill the equation:

\[ \rho = \frac{ZM}{N_A V} \]

where \( N_A \) is Avogadro's number. This equation was used to determine Z as:

\[ Z = \frac{N_A \rho V}{M} \]

This procedure is equivalent to the density argument presented on page 137. Although the density of the high-temperature phases is difficult to measure, the room temperature values are known (see section 6.2) and the density is not expected to change dramatically with temperature (density should decrease due to lattice expansion). Hence, Z was calculated using the room temperature density of SrFeO\textsubscript{x} and the results are presented in the table:

<table>
<thead>
<tr>
<th>x</th>
<th>Formula</th>
<th>M [g/mol]</th>
<th>( \rho ) [g/cm\textsuperscript{3}]</th>
<th>( V_{\text{PEROVSKITE}} ) [Å\textsuperscript{3}]</th>
<th>Z</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>Sr\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5}</td>
<td>366.93</td>
<td>4.99</td>
<td>63.14</td>
<td>0.52</td>
<td>Volume from Table A.6, T=1223K</td>
</tr>
<tr>
<td>2.75</td>
<td>Sr\textsubscript{4}Fe\textsubscript{4}O\textsubscript{11}</td>
<td>749.86</td>
<td>5.27</td>
<td>60.28</td>
<td>0.26</td>
<td>Volume from Table A.7, T=838K</td>
</tr>
</tbody>
</table>

The Z values obtained were substantially less than unity and the values were very close to \( \frac{1}{2} \) and \( \frac{1}{4} \) respectively. Fractional Z values clearly indicate that the "perovskite" cell, obtained by the direct indexing, is too small. In fact the "perovskite" cell constitutes an asymmetric unit.

The bigger cell (\( Fm\overline{3}c \)) was obtained by doubling of the perovskite lattice constant as described in the thesis. The \( Fm\overline{3}c \) unit cell contains whole number of molecules in the case of daltonian phases, \( \text{Sr}_2\text{Fe}_2\text{O}_5 \), \( \text{Sr}_4\text{Fe}_4\text{O}_{11} \) and \( \text{Sr}_8\text{Fe}_8\text{O}_{23} \), and assures electrical neutrality of the \( \text{Sr}_2\text{Fe}_2\text{O}_5 \) cell (see arguments on page 138).

\* Volume of the perovskite cell is equal to 1/8 of the \( Fm\overline{3}c \) unit cell volume.
The bigger *Fm3c* cell was chosen because it gives a proper description of the crystal structure and the chemical makeup of the compounds. The proposed cell allows a description of phases with intermediate compositions in terms of a solid solution of the daltonian phases as described in the thesis.

The *Pm3m* cell could be regarded as the unit cell only if we treat atoms as colour balls and neglect the fact that they are electrically charged when engaged in forming of a chemical compound.

5. *Questions concerning Equations (4.14-4.22).*

The experimental data did not allow the oxidation of SrFeO₅ to be examined over the entire composition range 2.5≤x≤3.0 nor an appropriate model to be developed. The composition range was limited to x≤2.75. Two cases were examined: a complete and a partial oxidation of Sr₂Fe₂O₅ to Sr₄Fe₄O₁₁ according to the chemical reaction (4.14).

In the case of complete oxidation the reactant and the product of the reaction are pure solids for which the activities are unity by definition. The equilibrium constant of the reaction is a function of oxygen partial pressure only (Equation (4.16)) [51]. However, this treatment of the oxidation reaction is artificial since a departure from the equilibrium conditions does not lead to a total conversion of Sr₄Fe₄O₁₁ back to Sr₂Fe₂O₅. This simplification was necessary to estimate the line of constant composition x=2.75 on the equilibrium composition diagram (Figure 4.6). This is also the reason why the equilibrium constant K given by Equation (4.15) does not go to 1/pO₂ when x→2.75 and activities of the solids are given by Equations (4.20-4.22).

In the case of partial oxidation we deal with a mixture/solution of two phases Sr₂Fe₂O₅ and Sr₄Fe₄O₁₁, which are in equilibrium with each other and the gas phase. Changes to temperature or partial pressure of oxygen only change the concentration (activities) of the two solids. In this case it was necessary to incorporate activities of solids into Equation (4.15) in order to calculate the equilibrium constant.

6. *Question concerning the phrase "Vacant oxygen sites" (p140 lines 11-12).*

The sentence referring to this aspect should be rephrased. The author meant that, since the oxygen sites are partially occupied at any given time, there must be an unoccupied site(s) somewhere in the crystal lattice. Since SrFeOₓ is an oxygen
conductor, diffusion (hopping) of oxygen between oxygen sites must be easier within
the (400) plane than in the perpendicular direction where oxygen sites are separated
by iron.

7. Question concerning a statement (p141 lines 5-7).

The author meant that crystal structure of any compound can be expressed in
terms of a lower symmetry group e.g. Triclinic P1 (which is true for every structure).
This approach is not elegant because we neglect all symmetry relationships in the
lattice but it is possible to propose. The sentence did not imply that a division of more
symmetric structures by eight would yield a primitive structure.

Additional Bibliography

Fe₂O₃ System. III. The Non-Existence of Single-Phase SrFe₂O₄. J. Magn.

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