Self Propagating High Temperature Synthesis of Ferrites in Magnetic Fields

Louise Affleck

University College London

A thesis submitted in accordance with the requirements of the University of London for the degree of Doctor of Philosophy

2002
Abstract

Self propagating high temperature synthesis (SHS) reactions have been performed on mixtures of BaO₂, Fe and Fe₂O₃ to form barium ferrite, BaFe₁₂O₁₉. Reactions were conducted in zero field and in an applied magnetic field of 1.1 T with the aim of exploring the influence of the field.

The temperature and velocity of the reactions were measured and the products, both post-SHS and post-annealing, were characterised by techniques including X-ray diffraction, Mössbauer spectroscopy, vibrating sample magnetometry and electron microprobe analysis. The applied magnetic field was found to lead to hotter and faster reactions, a greater degree of conversion of the reactants, a needle-like microstructure in the post-SHS product, and a reduced coercive field (~20-30 %) in the annealed product, compared to zero field. Sodium perchlorate was used as an internal oxidising agent, and found to produce similar effects. Correlations were observed between the temperature reached in the SHS reaction, the microstructure and reaction completeness of the post-SHS product and the magnetic parameters of the annealed product. One consequence is that it appears to be possible to control magnetic properties of the BaFe₁₂O₁₉ product by controlling the SHS conditions.

Reactions were also performed in magnetic fields of up to 20 T. Strongly and weakly magnetic systems in powder and pellet form were studied. Evidence was found to show that the magnetic field acts by reorganising strongly magnetic material along the field lines. Some evidence was found to suggest that the field affects weakly magnetic systems, so the field may also act by influencing ions at the SHS wavefront and/or by acting on paramagnetic oxygen.

The first time-resolved X-ray diffraction studies of SHS reactions to form ferrites, and the first such studies in a magnetic field, were performed. The experimental procedure was established and the important variables were determined. Reaction pathways were observed to be different in a magnetic field compared to zero field.
Acknowledgements

I must begin by thanking my supervisors, Ivan Parkin and Quentin Pankhurst. I am very grateful for the help, advice and encouragement they have given me during the course of my PhD and for making it such an enjoyable experience.

I wish to thank the following people from UCL who have helped me in various ways. Marco Agouas worked alongside me on SHS throughout our PhD projects, and I appreciated his good-humoured company and assistance. Warren Cross and Hayley Spiers worked with me during their undergraduate research projects. I enjoyed sharing a lab with them, along with Artur Nartowski, and more recently sharing an office with Helen Thompson and Jonathan Wasse. Daniel Ucko showed me how to use the VSM and Mössbauer equipment, and was a valued source of help and friendship. Other friends whose contribution I wish to acknowledge include Louise Price, Andrew Steer, Shusaku Hayama, Jonathan Allen and Eamonn Beime. Kevin Reeves performed the electron microprobe analysis measurements and assisted with the SEM and EDAX work. Maxim Kuznetsov gave me his expert advice on SHS during his visits to UCL and also performed the DTA/TGA measurements for me.

Outside of UCL I was helped by a number of people, who have my grateful thanks. Ann Terry of the ESRF and Dave Taylor of Daresbury Laboratory gave much kind and patient help with our TRXRD experiments, and my thanks extend to everyone who took part in the ESRF and Daresbury experiences. Marius Boamfa provided excellent support during my week at the Nijmegen High Field Magnet Laboratory. Melusine Colwell processed the Nijmegen spectrometer data into a useful format. Mark Green and Will Branford of the Royal Institution performed the electrical resistivity measurements on one of my samples.

One of the benefits of working in both the Chemistry and Physics departments has been the number of friends I have made. I want to thank them all for their kind help and encouragement and for making my time here such fun. I must also thank my friends outside of college whose caring support I have valued.

I want to thank my parents very much, for their constant love, generous support and gentle encouragement. I could not have done this without them.

My thanks would not be complete without thanking God (my heavenly Father), who made and sustains this intricate, ordered and fascinating world that it has been my privilege to study. He has guided and supported me in so many ways, for which I am very grateful.
Abstract .......................................................................................................................... 2
Acknowledgements ................................................................................................. 3
Table of Contents ........................................................................................................ 4
List of Tables .............................................................................................................. 9
List of Figures ............................................................................................................. 13

1 Introduction .............................................................................................................. 22
   1.1 Background .......................................................................................................... 22
   1.2 Self propagating high temperature synthesis (SHS) ........................................ 22
       1.2.1 SHS description .............................................................................................. 22
       1.2.2 Relevant parameters ....................................................................................... 25
       1.2.3 Solid state reactions ....................................................................................... 27
       1.2.4 Conventional ceramic synthesis ........................................................................ 29
       1.2.5 Advantages and disadvantages of SHS .......................................................... 31
   1.3 Ferrites ................................................................................................................ 32
       1.3.1 Spinels, garnets and hexagonal ferrites ......................................................... 32
       1.3.2 BaFe₁₂O₁₉ ...................................................................................................... 35
   1.4 Reactions in magnetic fields .................................................................................. 39
       1.4.1 Effect of magnetic fields on gas phase reactions .......................................... 39
       1.4.2 Effect of magnetic fields on liquid phase reactions ..................................... 42
       1.4.3 Effect of magnetic fields on solid phase reactions .................................... 43
   1.5 SHS in magnetic fields ......................................................................................... 43
       1.5.1 Effect of magnetic fields on pellet reactions ................................................. 45
       1.5.2 Explanations of magnetic field effects ............................................................ 46
       1.5.3 Relation of magnitude of field effect with Curie and combustion temperature .................................................................................................................... 47
       1.5.4 Direction of wave relative to magnetic field direction .......................... 48
   1.6 Generation of electric and magnetic fields by SHS ........................................... 50
   1.7 Previous work by the UCL group ................................................................. 52
   1.8 Overview ............................................................................................................. 53
2 Experimental .............................................................................................................. 57
  2.1 General experimental ....................................................................................... 57
  2.2 Green mixture preparations ........................................................................... 59
    2.2.1 Preparation of BaFe₁₂O₁₉ green mixture ............................................. 59
    2.2.2 Preparation of BaFe₁₂O₁₉ green mixture with sodium perchlorate ...... 60
  2.3 Performing SHS reactions .............................................................................. 60
    2.3.1 Reactions in zero field ............................................................................ 60
    2.3.2 Reactions in magnetic fields ................................................................... 61
    2.3.3 Green mixture compaction ...................................................................... 62
    2.3.4 Oxygen flow ............................................................................................ 63
    2.3.5 Point and bulk initiation ......................................................................... 63
  2.4 In-situ analysis of reactions ............................................................................ 64
    2.4.1 Temperature and velocity measurements .............................................. 64
    2.4.2 Time-resolved X-ray diffraction (TRXRD) .......................................... 64
    2.4.3 TRXRD – Daresbury Station 16.4 ......................................................... 65
    2.4.4 TRXRD – ESRF Beamline ID-11 ......................................................... 67
  2.5 Characterisation of products ......................................................................... 69
    2.5.1 X-ray diffraction (XRD) .......................................................................... 69
    2.5.2 X-ray diffraction at Daresbury Station 9.1 ........................................... 69
    2.5.3 Vibrating sample magnetometry (VSM) ................................................ 69
    2.5.4 Mössbauer spectroscopy ......................................................................... 70
    2.5.5 Scanning electron microscopy (SEM) / Energy dispersive X-ray
        analysis (EDAX) ...................................................................................... 70
    2.5.6 Electron microprobe analysis .................................................................. 71
    2.5.7 Thermal analysis .................................................................................... 71
  2.6 Summary ........................................................................................................... 71

3 The influence of processing parameters on SHS ............................................. 72
  3.1 Introduction ..................................................................................................... 72
    3.1.1 Green mixture parameters ...................................................................... 72
    3.1.2 SHS reaction parameters ...................................................................... 76
    3.1.3 SHS product parameters ...................................................................... 77
3.1.4 Ways to observe the influence of processing parameters .... 78

3.2 Experimental ............................................................................. 79
3.2.1 Reactant particle sizes ............................................................ 79
3.2.2 BaO₂ excess ......................................................................... 80
3.2.3 Oxygen source ..................................................................... 80
3.2.4 Oxygen flow rate ................................................................. 81
3.2.5 Annealing temperature and time ........................................... 82
3.2.6 Conventional ceramic synthesis ............................................. 83

3.3 Results ....................................................................................... 83
3.3.1 Reactant particle sizes ............................................................ 83
3.3.2 BaO₂ excess ......................................................................... 84
3.3.3 Oxygen source ..................................................................... 86
3.3.4 Oxygen flow rate ................................................................. 91
3.3.5 Annealing temperature and time ........................................... 94
3.3.6 Conventional ceramic synthesis ............................................. 96

3.4 Analysis and Discussion ............................................................... 98
3.4.1 Reactant particle sizes ............................................................ 98
3.4.2 BaO₂ excess ......................................................................... 99
3.4.3 Oxygen source .................................................................... 100
3.4.4 Oxygen flow rate ................................................................. 101
3.4.5 Annealing temperature and time ........................................... 102
3.4.6 Conventional ceramic synthesis ............................................. 102

3.5 Conclusions ............................................................................. 103

4 The influence of magnetic fields on SHS ..................................... 104
4.1 Introduction ............................................................................ 104
4.2 Experimental ........................................................................ 105
4.2.1 Reactions in zero field .......................................................... 105
4.2.2 Reactions in a 1.1 T magnetic field ....................................... 106
4.2.3 Pre-aligned reactions .......................................................... 107
4.2.4 Reactions on powders using perchlorate ............................. 108
4.2.5 Reactions on bars using perchlorate ................................... 108
4.2.6 Electrical resistivity measurements .................................... 109
4.2.7 Experiments at high magnetic field strengths ...................... 110

4.3 Results .......................................................................................... 116

4.3.1 Zero field reactions ................................................................. 125

4.3.2 1.1 T applied field reactions .................................................. 127

4.3.3 Pre-aligned reactions ............................................................... 129

4.3.4 Zero field reactions on powders using perchlorate ............... 131

4.3.5 1.1 T applied field reactions on powders using perchlorate ................................................................. 132

4.3.6 Pre-aligned reactions on powders using perchlorate ............ 133

4.3.7 Zero field reactions on pressed bar using perchlorate .......... 133

4.3.8 1.1 T applied field reactions on pressed bar using perchlorate ............................................................................ 135

4.3.9 Electrical resistivity measurements .................................... 136

4.3.10 Experiments at high magnetic field strengths .................... 137

4.4 Analysis and Discussion .............................................................. 145

4.4.1 Temperatures and velocities .................................................. 146

4.4.2 Shiny and matt parts / Reaction completeness ..................... 148

4.4.3 Reaction chemistry ................................................................. 150

4.4.4 420 kG Mössbauer component ............................................ 150

4.4.5 Needle-like microstructure ...................................................... 151

4.4.6 Magnetic properties of the products .................................... 152

4.4.7 Pre-aligned reactions ............................................................... 153

4.4.8 Use of internal oxidising agent, sodium perchlorate .......... 153

4.4.9 Electrical resistivity ................................................................. 155

4.4.10 Temperature measurements at high magnetic fields .......... 156

4.4.11 Influence of a magnetic field on strongly and weakly magnetic systems / Possible mechanisms for the influence of a magnetic field ....................................................................... 158

4.5 Conclusions ................................................................................ 161

5 Time-resolved X-ray diffraction studies ...................................... 163

5.1 Introduction ................................................................................ 163

5.2 Experimental .............................................................................. 166
5.2.1 TRXRD at Daresbury Station 16.4............................................. 168
5.2.2 TRXRD at ESRF Beamline ID-11 ........................................ 170

5.3 Results .................................................................................... 171
5.3.1 Fe/Fe₂O₃ ........................................................................... 171
5.3.2 Ba₆Fe₁₂O₁₉................................................................. 176

5.4 Analysis and Discussion .............................................................. 184
5.4.1 Fe/Fe₂O₃ ........................................................................... 184
5.4.2 Ba₆Fe₁₂O₁₉................................................................. 186
5.4.3 Fe/Fe₂O₃ and Ba₆Fe₁₂O₁₉ ............................................. 190
5.4.4 Reaction timescales ........................................................... 190
5.4.5 Reproducibility ................................................................. 191
5.4.6 Pellet reactions ................................................................. 192
5.4.7 Effect of a magnetic field as observed by TRXRD .......... 193
5.4.8 ESRF vs. Daresbury .......................................................... 194

5.5 Conclusions............................................................................ 194

6 Conclusions ............................................................................. 197

References ..................................................................................... 201

Publications and published abstracts .............................................. 209

Presentations (talks and posters) .................................................... 210
List of Tables

1 Introduction
Table 1.1 Ratio of iron oxide to metal oxide for the different types of ferrites. .................................................................32
Table 1.2 Descriptions of different types of hexagonal ferrites .........................................................35
Table 1.3 Fe$^{3+}$ sublattices in BaFe$_{12}$O$_{19}$ .............................................................37

2 Experimental
Table 2.1 Details of the reagents used in the SHS reactions .........................................................57

3 The influence of processing parameters on SHS
Table 3.1 Amounts of the reagents used in green mixtures with different amounts of BaO$_2$ excess .........................................................80
Table 3.2 Phase composition of barium ferrite furnace-reacted (bulk initiated) products produced with different sizes of Fe particles. Furnace reaction includes partial annealing .........................................................84
Table 3.3 Amounts of impurity phases in annealed products as a function of BaO$_2$ excess in BaFe$_{12}$O$_{19}$ green mixture, identified by XRD and Mössbauer analysis .........................................................85
Table 3.4 Influence of different oxygen sources on the temperature, colour and velocity of the SHS wave for reactions on barium ferrite green mixture in zero field (ZF) and 1.1 T applied field (AF) .........................................................87
Table 3.5 Influence of oxygen source on the magnetic parameters of the annealed BaFe$_{12}$O$_{19}$ products .........................................................90
Table 3.6 Effect of oxygen flow rate on the reaction temperature, velocity, time taken to react, and mass of shiny part in the product, for zero field (ZF) and 1.1 T applied field (AF) barium ferrite reactions...92
Table 3.7 Effect of oxygen flow rate on the magnetic parameters of the annealed BaFe$_{12}$O$_{19}$ products .........................................................93
Table 3.8  Phases observed for different annealing temperatures and times of barium ferrite post-SHS products.................................................................94

Table 3.9  Comparison of Mössbauer parameters for BaFe$_{12}$O$_{19}$ products made by SHS and by conventional ceramic synthesis. The SHS product was annealed at 1150 °C for 6 hours; the ceramic synthesis product was heated to 1200 °C for 2 hours. Isomer shift $\delta \pm 0.01$ mm s$^{-1}$, quadrupole shift $2\varepsilon \pm 0.02$ mm s$^{-1}$, linewidth $\Gamma \pm 0.01$ mm s$^{-1}$, hyperfine field $B_{hf} \pm 1$ kG........................................97

Table 3.10  Comparison of magnetic parameters for BaFe$_{12}$O$_{19}$ products made by SHS and by conventional ceramic synthesis. The SHS product was annealed at 1150 °C for 6 hours; the ceramic synthesis product was heated to 1200 °C for 2 hours....................................................97

4  The influence of magnetic fields on SHS

Table 4.1  Reactions performed at variable magnetic field strengths at Nijmegen High Field Magnet Laboratory.................................111

Table 4.2  Reaction temperature and velocity and description of products, for reactions performed on barium ferrite green mixture in different conditions. .................................................................117

Table 4.3  XRD data for post-SHS and annealed barium ferrite products prepared under different reaction conditions. Products were annealed at 1150 °C for 6 hours or 1200 °C for 2 hours. Products made with perchlorate were also washed prior to analysis ........118

Table 4.4  Mössbauer parameters for post-SHS barium ferrite non-perchlorate products. Isomer shift $\delta \pm 0.01$ mm s$^{-1}$, quadrupole splitting $\Delta \pm 0.02$ mm s$^{-1}$, quadrupole shift $2\varepsilon \pm 0.02$ mm s$^{-1}$, linewidth $\Gamma \pm 0.01$ mm s$^{-1}$, hyperfine field $B_{hf} \pm 1$ kG. Values shown in red were fixed during the fitting process.........................................................120

Table 4.5  Mössbauer parameters for post-SHS barium ferrite perchlorate products. Isomer shift $\delta \pm 0.01$ mm s$^{-1}$, quadrupole splitting $\Delta \pm 0.02$ mm s$^{-1}$, quadrupole shift $2\varepsilon \pm 0.02$ mm s$^{-1}$, linewidth $\Gamma \pm 0.01$
mm s\(^{-1}\), hyperfine field \(B_{hf} \pm 1\) kG. Values shown in red were fixed during the fitting process.

Table 4.6 Mössbauer parameters for annealed \(\text{BaFe}_{12}\text{O}_{19}\) products, fitted with relative areas in the ratio 12:6:4:1.5. Products were annealed at 1150 °C for 6 hours or 1200 °C for 2 hours. Isomer shift \(\delta \pm 0.01\) mm s\(^{-1}\), quadrupole shift \(2\varepsilon \pm 0.02\) mm s\(^{-1}\), linewidth \(\Gamma \pm 0.01\) mm s\(^{-1}\), hyperfine field \(B_{hf} \pm 1\) kG. Values shown in red were fixed during the fitting process.

Table 4.7 Magnetic parameters for \(\text{BaFe}_{12}\text{O}_{19}\) products made under different reaction conditions, annealed at 1150 °C for 6 hours or 1200 °C for 2 hours. Products made with perchlorate were also washed prior to analysis.

Table 4.8 Approximate phase composition (volume %) of post-SHS products from \(\text{BaFe}_{12}\text{O}_{19}\) reactions at different magnetic field strengths up to 20 T, determined by X-ray diffraction.

Table 4.9 Magnetic parameters for post-SHS products from \(\text{BaFe}_{12}\text{O}_{19}\) reactions on powders and pellets at different magnetic field strengths up to 20 T.

Table 4.10 Curie temperatures for phases involved in SHS reactions to form \(\text{BaFe}_{12}\text{O}_{19}\) (from Landolt-Börnstein and Handbook of Chemistry and Physics).

5 Time-resolved X-ray diffraction studies

Table 5.1 Time-resolved X-ray diffraction experiments performed.
Table 5.2 Equivalent 2\(\theta\) ranges for the detectors at Daresbury and ESRF.
Table 5.3 Comparison of the experiment specifications between Daresbury and ESRF.
Table 5.4 Daresbury detector details, required for data processing.
Table 5.5 Region of best response for each detector at Daresbury Station 16.4.
Table 5.6  \textbf{BaFe}_{12}\text{O}_{19} reaction timescales, estimated from time-resolved X-ray diffraction data.} 182
List of Figures

1 Introduction

Figure 1.1 Diagram of an SHS propagation wave: (a) the green mixture is ignited at one end, (b) a propagation wave proceeds through the green mixture. Reacted material is formed behind the wave. ........23

Figure 1.2 Plot showing the regions predicted for SHS to occur, from Eqn. 1.4, compared with experimental results: ● no SHS, O SHS (from Bowen and Derby). .................................................................27

Figure 1.3 Spinel structure. One AB$_2$O$_4$ formula unit is shown – eight of these make up the unit cell. Only the front tetrahedral sites and the top face and centre octahedral sites are shown; there are effectively eight tetrahedral and four octahedral sites in this cube (from Parish). ....................................................................................33

Figure 1.4 Compositional diagram for BaO-MO-Fe$_2$O$_3$. The letters M, U, W, X, Y and Z denote different types of hexagonal ferrite (from Landolt-Börnstein). The letter F represents BaFe$_2$O$_4$ (which has a structure similar to BaAl$_2$O$_4$) and S represents a spinel ferrite. ......35

Figure 1.5 (a) BaFe$_{12}$O$_{19}$ crystal structure. The unit cell is shown; it consists of two formula units (from Valenzuela). (b) The exchange interactions between the spins of the Fe$^{3+}$ ions in the different sites in the BaFe$_{12}$O$_{19}$ structure. This illustrates the ferrimagnetic nature of barium ferrite (from Kojima). .........................................................36

Figure 1.6 Diagram of experiments on diffusion flames in different positions relative to a gradient magnetic field (from Wakayama and Sugie). ... .................................................................40

Figure 1.7 Photographs of flames with fuel gas flowing towards decreasing field strength (at position A): (a) flame in zero field, (b) flame in gradient magnetic field of 0.35 T cm$^{-1}$ (from Wakayama and Sugie). .................................................................40
2 Experimental

Figure 2.1 An SHS propagation wave in zero field, for the reaction of a powder mixture of BaO₂ + Fe + Fe₂O₃ under a flow of oxygen. The strip of powder is ~8 cm long. The reaction proceeds from right to left. Photographs were taken at t = 5 s (bottom), t = 20 s (middle) and t = 35 s (top)
3 The influence of processing parameters on SHS

Figure 3.1 Reaction rate vs. metal particle diameter for a variety of SHS reactions (from Rice). ..................................................73

Figure 3.2 Relationship between relative particle sizes and contact between different particles (from Bowen and Derby): (a) small carbon particles (carbon black), (b) larger carbon particles (graphite). .....74

Figure 3.3 Reaction rate vs. theoretical density of reactant compact (from Rice). (The numbers in brackets refer to the particle sizes, in μm, of the cations and anions). ..................................................75

Figure 3.4 Set-up for oxygen flow rate experiments in a 1.1 T magnetic field... ..................................................82

Figure 3.5 XRD patterns of annealed barium ferrite applied field (shiny) products, made with (a) zero % and (b) 5 % excess of BaO₂ .....85

Figure 3.6 TGA (top) and DTA (bottom) plots for the reaction of Fe + Fe₂O₃ (black) and BaO₂ + Fe + Fe₂O₃ (red), in air. ......................86

Figure 3.7 Photographs of barium ferrite SHS products from: (a) zero field powder reaction, (b) 1.1 T powder reaction, side view, (c) 1.1 T powder reaction, end view of hourglass shape, (d) zero field powder reaction with sodium perchlorate as internal oxygen source, (e) 1.1 T reaction with sodium perchlorate, (f) zero field bar reaction with sodium perchlorate (1.1 T bar looked identical). .....88
4  The influence of magnetic fields on SHS

Figure 4.1  Green mixture in 1.1 T applied magnetic field, adopting an hourglass shape ................................................................. 107

Figure 4.2  Pre-aligned green mixture adopting a pseudo hourglass shape.... 108

Figure 4.3  Alignment of pressed bar of green mixture in 1.1 T magnetic field. The long axis of the bar is parallel to the tube axis ............... 109

Figure 4.4  Resistivity measurements set-up. The current is supplied via the two outer contacts, and the voltage is measured across the two inner contacts ................................................................. 110

Figure 4.5  Pellet reactions in high magnetic fields up to 20 T at Nijmegen High Field Magnet Laboratory: (a) diagram of experimental set-up in magnet, (b) photograph of quartz tube showing optical fibre and oxygen inlet connections ......................................................... 114

Figure 4.6  Close-up view of pellet ignition for high magnetic field reactions. ........................................................................................................ 114
Figure 4.7 Powder reactions in high magnetic fields up to 20 T at Nijmegen High Field Magnet Laboratory: (a) diagram of experimental set-up in magnet, (b) photograph of powder cell showing suspension wires and oxygen inlet tube.

Figure 4.8 Photograph of inside of powder reaction cell, for high magnetic field reactions. The lid is shown on the left; the two holes in the centre are where the ignition wire comes through into the cell.

Figure 4.9 Plot of the $a$ and $c$ lattice parameters of the BaFe$_{12}$O$_{19}$ washed and annealed products, grouped into categories related to the synthesis conditions. Also plotted are the literature values for BaFe$_{12}$O$_{19}$.

Figure 4.10 Plot of the relative areas of each phase within the different post-SHS products, from Mössbauer spectroscopy. The plotting order of the samples is chosen to show the progression in combustion completeness.

Figure 4.11 Magnetic hysteresis loops for selected annealed BaFe$_{12}$O$_{19}$ products.

Figure 4.12 Plot of the measured maximum magnetisation vs. coercive field values for the BaFe$_{12}$O$_{19}$ washed and annealed products, grouped into categories related to the synthesis conditions.

Figure 4.13 Product from the zero field reaction of BaO$_2$ + Fe + Fe$_2$O$_3$ + oxygen flow.

Figure 4.14 Electron microprobe composition maps of the microstructures of the post-SHS products from the reaction of BaO$_2$ + Fe + Fe$_2$O$_3$ + oxygen flow in (a) zero field, (b) 1.1 T applied field (shiny part).

Figure 4.15 Photographs of an SHS reaction in a 1.1 T applied magnetic field. The magnetic field direction is vertical and the hourglass shape adopted by the mixture can be seen. Times shown are from the time the reaction was ignited, $t = 0$ s. The reaction is of BaO$_2$ + Fe + Fe$_2$O$_3$ in an oxygen flow of 2 l min$^{-1}$. The photographs were taken from video camera footage.
Figure 4.16 Products from the 1.1 T applied field reaction of BaO\(_2\) + Fe + Fe\(_2\)O\(_3\) + oxygen flow: (a) side view, (b) end view, which shows the hourglass shape of the product, (c) internal structure showing predominantly grey fibres. The shiny fibrous macrostructure can be seen in these photographs.................................................. 128

Figure 4.17 Products from the pre-aligned reaction of BaO\(_2\) + Fe + Fe\(_2\)O\(_3\) + oxygen flow: (a), (b) side views showing shiny fibrous structure along field direction, (c) end view showing pseudo-hourglass shape, (d) internal structure – mainly grey rather than shiny...... 130

Figure 4.18 Product from the zero field reaction of a powder mixture of BaO\(_2\) + Fe + Fe\(_2\)O\(_3\) + perchlorate................................................................. 131

Figure 4.19 Product from the 1.1 T applied field reaction of a powder mixture of BaO\(_2\) + Fe + Fe\(_2\)O\(_3\) + perchlorate................................................................. 132

Figure 4.20 Product from the zero field reaction of a pressed bar of BaO\(_2\) + Fe + Fe\(_2\)O\(_3\) + perchlorate................................................................. 134

Figure 4.21 Electron microprobe composition maps of the microstructures of the post-SHS products from the reaction of pressed bars of BaO\(_2\) + Fe + Fe\(_2\)O\(_3\) + perchlorate in (a) zero field, (b) 1.1 T applied field................................................................. 134

Figure 4.22 Plot of ln (resistivity) vs. 1/temperature for a shiny piece of a barium ferrite post-SHS product. The lines in red are extrapolations to determine the gradient................................................................. 137

Figure 4.23 Barium ferrite post-SHS products from pellets reacted in magnetic field strengths of 0, 5, 10, 15 and 20 T................................................................. 138

Figure 4.24 Internal structure of a barium ferrite pellet reacted at 15 T....... 138

Figure 4.25 Barium ferrite post-SHS products from powders reacted in magnetic field strengths from 0 to 20 T................................................................. 139

Figure 4.26 Strontium titanate post-SHS products from pellets reacted in magnetic field strengths of 0, 5, 10, 15 and 20 T................................................................. 140

Figure 4.27 Spectrometer data (intensity vs. wavelength) from the reaction of a pellet to form barium ferrite in different magnetic field strengths:
(a) 0 T, (b) 5 T, (c) 10 T, (d) 15 T and (e) 20 T. The spectra collected at different time intervals are overlaid.

Figure 4.28 Spectrometer data (intensity vs. wavelength) from the reaction of a pellet to form barium titanate in different magnetic field strengths: (a) 0 T, (b) 5 T. The spectra collected at different time intervals are overlaid.

Figure 4.29 Plots of the spectrometer data from the Nijmegen high magnetic field reactions on pellets of: (a), (b) BaFe$_{12}$O$_{19}$ and (c), (d) BaTiO$_3$. The wavelength of the peak attributed to the SHS reaction is plotted vs. time in (a) and (c); the normalised intensity of this peak is plotted vs. time in (b) and (d).

Figure 4.30 Reaction scheme for the reaction of BaO$_2$ + Fe + Fe$_2$O$_3$ + O$_2$ to form BaFe$_{12}$O$_{19}$. Phases identified in the post-SHS products are shown in boxes (BaO falls below the detection limits of the equipment used).

Figure 4.31 Flow diagram of effects due to a magnetic field and use of an internal oxidising agent (sodium perchlorate).

5 Time-resolved X-ray diffraction studies

Figure 5.1 Fe/Fe$_2$O$_3$ zero field powder reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown).

Figure 5.2 Fe/Fe$_2$O$_3$ 0.2 T powder reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown).

Figure 5.3 Daresbury data (scan number vs. energy) for Fe/Fe$_2$O$_3$ powder reactions: (a), (b) zero field; (c) 0.2 T; (d) 1.1 T.

Figure 5.4 Diffraction ring patterns recorded at ESRF, for Fe/Fe$_2$O$_3$ reactions of powders. (a) Green mixture pattern, recorded in 0.2 T field, (b)-(e) patterns recorded in situ during the reactions: (b) zero field, (c) 0.2 T field, (d) close-up view of the zero field pattern, (e) close-up view of the 0.2 T pattern. Spots appear in some of the rings during the reaction.
Figure 5.5 Single scan diffraction patterns of the post-SHS products from Fe/Fe$_2$O$_3$ reactions of powders in (a) zero field and (b) 0.2 T, recorded at ESRF. .................................................................175

Figure 5.6 BaFe$_{12}$O$_{19}$ zero field powder reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown). Some of the main peaks for each phase are labelled. .................................................................176

Figure 5.7 BaFe$_{12}$O$_{19}$ 0.2 T powder reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown). Note that in this figure the first scan is at the front (opposite orientation to the other figures). .................................................................177

Figure 5.8 BaFe$_{12}$O$_{19}$ 1.1 T powder reaction, Daresbury July 99 data (middle detector). The numbers on the right hand side are the scan numbers. Each scan was recorded for 250 ms and the time between each scan is 2 s. .................................................................178

Figure 5.9 BaFe$_{12}$O$_{19}$ 1.1 T pellet reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown). .................................................................178

Figure 5.10 2D plots (scan number vs. energy) for BaFe$_{12}$O$_{19}$ 1.1 T powder reaction, Daresbury July 99 data: (a) middle detector, (b) top detector. The brighter colours indicate the more intense peaks. .................................................................179

Figure 5.11 3D plots (scan number, energy, intensity) for BaFe$_{12}$O$_{19}$ 1.1 T powder reaction, Daresbury July 99 data: (a) middle detector, (b) top detector. .................................................................179

Figure 5.12 Daresbury data (scan number vs. energy) for BaFe$_{12}$O$_{19}$ reactions: (a), (b) zero field (powders); (c), (d) 0.2 T (pellets); (e)-(h) 1.1 T (e, f, g - powders, h - pellet). .................................................................180

Figure 5.13 BaFe$_{12}$O$_{19}$ zero field powder reaction, ESRF data, 50 ms per scan (every 2 scans shown). In this reaction region plot, the diffraction patterns for the starting material and the products are shown in red and the number of scans between them is used to estimate the reaction timescale. .................................................................181

Figure 5.14 Diffraction ring pattern recorded at ESRF in situ during the zero field powder reaction of BaO$_2$ + Fe + Fe$_2$O$_3$ + O$_2$: (a) complete
zero field pattern, (b) close-up of (a). The rings are sharp and do not contain many spots.................................................................182

Figure 5.15 Single scan diffraction patterns of the post-SHS products from BaFe$_{12}$O$_{19}$ reactions on pellets and powders in (a) zero field, (b) 0.2 T and (c) 1.1 T, recorded at ESRF.................................................................183

Figure 5.16 Relative abundance of each phase vs. time, for the powder reaction of Fe + Fe$_2$O$_3$ + O$_2$, in zero field, determined by analysis of TRXRD results. Fe$_{1-x}$O, wüstite, is observed as an intermediate phase.................................................................184

Figure 5.17 Reaction scheme for the reaction of Fe + Fe$_2$O$_3$ in the presence of oxygen........................................................................185

Figure 5.18 BaFe$_{12}$O$_{19}$ 1.1 T reaction, Daresbury July 99 data (middle detector), 250 ms per scan, 2 s between scans (2D plot of time vs. energy); (a) complete data set of 70 scans, (b) close-up showing curvature of peaks. This plot shows the curvature of peak positions towards higher energies, or smaller d-spacings, i.e. lattice contraction. ...188

Figure 5.19 Change in d-spacing vs. time for BaFe$_{12}$O$_{19}$ 1.1 T reaction, Daresbury July 99 data. This plot shows that the lattice takes ~45-60 s to contract to its final value after the SHS wave has passed. ....................................................................................................189
1 Introduction

1.1 Background

Self propagating high temperature synthesis, or SHS, describes highly exothermic solid state reactions that proceed via a propagation or combustion wave. It was discovered in the late 1960s by Merzhanov and co-workers and has been used to synthesise a variety of materials. Familiar examples of SHS include the Goldsmidt reaction (Eqn. 1.1) which is used to produce chromium and the Thermite reaction (Eqn. 1.2) which is used in welding.

\[
\text{Cr}_2\text{O}_3 + \text{Al} \rightarrow \text{Cr} + \text{Al}_2\text{O}_3 \quad \text{Eqn. 1.1}
\]

\[
\text{Fe}_2\text{O}_3 + \text{Al} \rightarrow \text{Fe} + \text{Al}_2\text{O}_3 \quad \text{Eqn. 1.2}
\]

SHS can be used to produce a wide range of materials, including nitrides, borides, carbides and oxides. One class of materials of particular interest that can be made by SHS is the ferrites. Ferrites are magnetic iron oxides which are used in several commercial applications, such as permanent magnets in motors and loudspeakers, and for magnetic recording media.

The aim of the work in this thesis is to seek to understand how applied magnetic fields influence SHS reactions to form ferrites, and how this might be used to influence product microstructure and thereby technologically important properties such as the magnetic figures of merit.

1.2 Self propagating high temperature synthesis (SHS)

1.2.1 SHS description

SHS or self propagating high temperature synthesis describes reactions which self propagate due to their high exothermicity. Once the reaction has been initiated no external heating is required. High temperatures are reached, typically in excess of
1000 °C. Not every exothermic reaction will self propagate. All solid state exothermic reactions generate heat, but only SHS reactions generate enough heat to result in a propagation wave. An SHS reaction is a particular type of exothermic reaction, in which the exothermicity is greater than a critical value so that the reaction self propagates.

An SHS reaction can be started in two ways. If initiated at a point it proceeds via a propagation wave, also known as a synthesis or combustion wave. A diagram of an SHS wave is shown in Figure 1.1. This wave is the “flame”, the combustion front, and is the interface between the unreacted and reacted material. Alternatively the reaction may be initiated in bulk, known as the “thermal explosion” method. In this case, the reactants are heated in a furnace. When the ignition temperature is reached, the reaction is initiated simultaneously at many sites throughout the green mixture.

![Diagram of an SHS wave](image)

**Figure 1.1 – Diagram of an SHS propagation wave:** (a) the green mixture is ignited at one end, (b) a propagation wave proceeds through the green mixture. Reacted material is formed behind the wave.

The propagation wave may proceed through the green mixture in different ways. There are stable and unstable modes of propagation. In the stable mode, the wave front is planar and moves with a constant velocity from layer to layer through the material. There are two unstable modes of propagation, oscillating and spinning. In the oscillating (or pulsating) mode, the planar wave front moves from layer to layer but its velocity is not uniform. Instead it moves in a series of stops and starts. In the spinning mode, the wave front moves with a uniform velocity, but it is not planar. Instead it moves as a hot spot along a defined path, for example, along a spiral path, hence the name spinning. If there are many such hot spots the
wave front can appear as fingers. The mode of propagation depends on the particular reaction. Solid-solid reactions tend to proceed with a stable mode.

The mode of propagation can affect the microstructure of the product. For example, the oscillating mode can produce a layered microstructure, whereas spinning can result in just the surface layer reacting.

SHS systems fall into two main types: homogeneous and heterogeneous systems. Homogeneous systems are those where the reactants are all in the same physical state, for example, they are all solids (powders). These are also known as solid-solid or gasless combustion systems. For a true homogeneous system, gases will not take part in the reaction and none of the solid phases will melt during the synthesis. A “solid flame” describes the propagation wave in a reaction that takes place solely between solid reactants. Heterogeneous systems comprise reactants in different states, typically solids and gases. These are also known as solid-gas, filtration, permeation or hybrid combustion systems.

There are two mechanisms of SHS: equilibrium and non-equilibrium. The difference between them is the stage at which the structure of the product is formed. In the equilibrium mechanism, the product structure is formed in the SHS wave. The structure forms in the same region and at the same time as the reaction happens. The requirement for the equilibrium mechanism is that the crystallisation and recrystallisation processes occur much faster than the reaction itself, i.e.: \( t_r \gg t_c, t_{rec} \), where \( t_r \) = time for the reaction, \( t_c \) = crystallisation time, \( t_{rec} \) = recrystallisation time. In the non-equilibrium mechanism, structural transformations happen in the region behind the wave. The chemical reactions have been completed but changes continue in the post-wave zone. The requirement for the non-equilibrium mechanism is that the reaction occurs much more quickly than the crystallisation and recrystallisation processes, i.e.: \( t_r << t_c, t_{rec} \).
1.2.2 Relevant parameters

There are certain parameters quoted in the SHS literature that are useful to characterise the reactions. The most important parameters are the ignition temperature, adiabatic combustion temperature and reaction velocity.

The ignition temperature, \( T_{ig} \), is the temperature at which a thermal explosion occurs,\(^5\) i.e. the temperature at which the reaction initiates. It is a quantity that is measured experimentally, either by thermocouples, differential thermal analysis or by noting the furnace temperature in a thermal explosion. At the ignition temperature the reaction rate increases rapidly. It is only really defined for thermal explosions, and does not apply for oxidation reactions.\(^10\) Typical ignition temperatures are in the range \(-900-1500\) K.\(^11\)

The adiabatic combustion temperature, \( T_{ad} \), is the maximum theoretical temperature reached by the products during the reaction, assuming adiabatic conditions.\(^4\) If the reaction enthalpy heats up the products without loss of heat to the surroundings, the adiabatic combustion temperature can be calculated using Eqn. 1.3,

\[
-\Delta H_{r,298K} = \int_{298K}^{T_{ad}} C_p(\text{products})dT
\]

where \(-\Delta H_{r,298K}\) is the reaction enthalpy at 298 K, \( C_p(\text{products}) \) is the total heat capacity of the products and \( T_{ad} \) is the adiabatic combustion temperature.

Yi and Moore\(^4\) state that it is reasonable to assume adiabatic conditions for SHS because there is very little time for heat to be lost to the surroundings, due to the fast nature of SHS. However, measured combustion temperatures, \( T_c \), are often several hundreds of degrees lower than \( T_{ad} \) due to significant heat losses. Still, \( T_{ad} \) is a useful parameter to characterise SHS reactions because it gives an indication of \( T_c \) and it can be calculated from a knowledge of \(-\Delta H_{r,298K}\) and \( C_p(\text{products}) \).
Non-adiabatic conditions are those where there is heat loss to the surroundings. If the heat loss is too great the reaction will fail to propagate. The initial temperature implied in Eqn. 1.3 is 298 K, although some reactions require preheating.\(^5\)\(^11\)

The reaction velocity is another important parameter. It is defined as the average velocity of the propagation wave. The instantaneous velocity will vary for the unstable oscillating mode of propagation. The actual value of the velocity is of no particular importance. Instead, velocity measurements are compared — the dependence of the velocity on various parameters gives useful information on the SHS process. Typical velocities are 0.1-10 cm s\(^{-1}\).

The exothermicity of the reaction is a crucial factor in SHS. Typical exothermicities are of the order of 500 kJ mol\(^{-1}\). Higher exothermicity tends to lead to greater reaction temperatures and velocities.

The requirements for SHS have been defined from both experiment and theory. Novikov \textit{et al.}\(^12\) found from experiment that for SHS to occur, \(T_{ad} > 1800\) K. This has been alternatively expressed by Munir\(^13\) as \(\Delta H_{r,298K} / C_p,298K \geq 2000\) K. These relations were for homogeneous reactions where the reactants do not melt, so it is not clear that they would apply to heterogeneous systems. From theory, Bowen and Derby\(^11\) found that for SHS to occur,

\[
\frac{T_{ad} - T_{ig}}{T_{ig} - T_{start}} \geq \frac{\overline{C_p}(\text{reactants})}{\overline{C_p}(\text{products})}
\]  

Eqn. 1.4

where \(T_{ad}\) is the adiabatic combustion temperature, \(T_{ig}\) is the ignition temperature (the temperature at which the reaction initiates), \(T_{start}\) is the initial temperature of the reactants, usually 298 K although it may be raised by preheating, \(\overline{C_p}(\text{reactants})\) is the mean specific heat between \(T_{start}\) and \(T_{ig}\), and \(\overline{C_p}(\text{products})\) is the mean specific heat between \(T_{ad}\) and \(T_{ig}\).
This relation (Eqn. 1.4) was found by considering a finite difference model, using the requirement that for SHS enough heat must be released by the reaction to ignite the reactants ahead of the reaction zone. Heat losses out of the reacting cell were neglected. Although it does not include parameters such as density and thermal conductivity, Eqn. 1.4 agrees well with experimental results in determining whether or not a given reaction will undergo SHS, as the plot in Figure 1.2 shows.

![Figure 1.2 - Plot showing the regions predicted for SHS to occur, from Eqn. 1.4, compared with experimental results: • no SHS, ○ SHS (from Bowen and Derby)\(^1\).](image)

1.2.3 Solid state reactions

In a typical solid state reaction, the reactant powders are mixed together and heated at high temperature for a length of time. High temperatures are needed to decompose the starting materials and to overcome the solid state diffusion barrier. Diffusion in solids is a slow process, but for a reaction to happen, the atoms or ions must diffuse through the particles and across the interfaces between particles. Heating increases the rate of diffusion, and if one of the reactants melts the atoms or ions are much more able to diffuse. If it is ions that are involved, the cations are
generally smaller and more mobile than the anions, so it is the cations that will
diffuse across the interfaces. As well as increasing the reaction temperature, there
are other ways to increase the reaction rate of solid state reactions. These include
increasing the number of reaction interfaces, by pelletizing to reduce the void
space between particles; reducing the particle size to increase the total surface
area and reduce diffusion distances; and thorough grinding of the starting
materials to ensure homogeneous mixing. During the reaction a product layer
builds up between the reactants, so regrinding introduces fresh reactant surfaces.

SHS is a type of solid state reaction. There are many processes that occur in solid
state reactions. The particle surfaces are where the reaction begins. On an atomic
scale, the atoms or ions are in contact, and gases may adsorb onto the surfaces.
Chemical reaction takes place which releases heat due to the exothermic nature of
the reaction. Small crystals of the new product are nucleated. Particles are thus
fused together with a layer of product between them. For further reaction to occur,
atoms or ions must diffuse through the reactant particles and across the product
layer. Heat transport will also be important for the reaction. The heat generated by
the reaction may cause physical changes such as reactants melting or
decomposing. It will also cause the lattices of the reactants and products to expand
(since most materials have a positive coefficient of thermal expansion).

"Structural macrokinetics"\textsuperscript{6,9} is a term that describes the kinetics of structural
changes during SHS, as well as chemical kinetics and theories of heat and mass
transfer. It is used for the non-equilibrium mechanism of SHS, where structural
transformations happen in the region behind the wave. It includes a number of
processes which occur during SHS: the reaction may form an amorphous product
or melt, that would then crystallise to form an intermediate crystalline product
with a non-equilibrium structure, then a final crystalline product with an
equilibrium structure.\textsuperscript{6,9}

Combustion is defined as the reaction with oxygen to form oxides. Oxidation and
reduction is inherent in combustion, since the formation of the oxide product is
the driving force for the reaction. SHS theory deviates from combustion theory because a non-equilibrium mechanism is possible, i.e. the product structure does not necessarily form in the SHS wave.

A subset of SHS is Solid State Metathesis (SSM). The driving force of SSM reactions is the lattice energy of the co-produced salt. An example of a SSM reaction is given in Eqn. 1.5,

\[
\text{Li}_n\text{N} + \text{MCl}_n \rightarrow \text{MN} + n\text{LiCl} \quad \text{Eqn. 1.5}
\]

where M is a metal. SSM is different to SHS, because the combustion temperatures tend to be lower in SSM, and the co-produced salt acts as a heat brake.

Materials that can be made by SHS include metal nitrides, borides, carbides, silicides, hydrides, oxides, intermetallic alloys, composites, electronic materials, refractories, abrasives, lubricants and a wide range of ceramics. The most commonly studied systems are those between elements, such as Ti-B, Ta-C and Mo-Si, since these are simple systems. Comparatively little research has been published on the synthesis of oxide materials by SHS. Oxides that have been made by SHS include perovskites (ABO₃), spinels (AB₂O₄) for use as catalysts, complex oxides, and high temperature superconductors such as YBa₂Cu₃O₇₋ₓ.

1.2.4 Conventional ceramic synthesis

The standard ceramic processing route to form magnetic iron oxides, or ferrites, involves several grinding, mixing and heating cycles. For example, to form barium ferrite, BaFe₁₂O₁₉, simple oxides such as barium carbonate, BaCO₃, and iron oxide, Fe₂O₃, are used as starting materials. They are heated together at 1000-1250 °C for several hours to produce the ferrite phase. The product powder is ground and mixed to maximise the number of reaction interfaces, then reheated to ensure complete reaction. Further processing may include the addition of binders, wet pressing, drying and sintering to form bonded, shaped products.
Disadvantages of the ceramic method include the costs associated with long heating times to high temperatures, contamination from the furnace, and the trial and error nature of finding good reaction conditions, since the progress of the reaction cannot be monitored.

To overcome the problems with the traditional ceramic processing method, a number of other solid state synthetic routes have been developed. Important commercial routes include glass crystallisation\textsuperscript{21,22,23} and chemical co-precipitation\textsuperscript{24,25}

In the glass crystallisation method,\textsuperscript{21,22,23} the raw materials are mixed, heated to form a melt, then cooled rapidly to produce amorphous glass flakes. These flakes are heated to produce a crystalline product phase, then the extra material is dissolved away to leave uniform fine particles of the ferrite phase. Since a melt is produced, the ions are highly mobile and have high diffusion rates, leading to fast reaction times. Fine, crystalline particles of the product may be produced with control over their size and shape.\textsuperscript{21} However, this method is quite involved chemically.

Chemical co-precipitation\textsuperscript{24,25} involves mixing an aqueous solution of the ions that are required in the final product with an alkaline solution. Precipitates form, which are filtered off, washed, dried, and mixed with salts. Upon heating, fine particles of the product crystallise out from the salt matrix. The advantage of this method is that the ions are mixed on the atomic scale, so very homogeneous mixtures are produced. However, it can be difficult to achieve the desired stoichiometry with this method, since some ions can be left in solution.\textsuperscript{24,25} Again, this route is not simple.

The goal in ferrite production is usually to produce small, crystalline particles, since such particles have the best magnetic properties. This goal is difficult to achieve; formation of small particles requires low synthesis temperatures, but this does not lead to high crystallinity. High temperatures give good crystallinity, but
large particles because grain growth is promoted. The standard ceramic route attempts to overcome this by limiting the time spent at the highest temperature.\textsuperscript{20} In glass crystallisation and chemical co-precipitation the particles are trapped in a matrix, so heating produces crystallinity without grain growth.\textsuperscript{21,25}

1.2.5 Advantages and disadvantages of SHS

SHS provides many advantages compared to standard ceramic processing methods. SHS reactions are quicker and cheaper than the standard processing methods; the reactions are fast, involve a small number of steps and do not require any external heating from furnaces. Expensive pure starting materials are not necessary since impurities are often expelled in the reactions, due to the high temperatures reached. Also, contamination from the furnace is largely avoided. The rapid heating and cooling rates involved lead to high concentrations of defects and metastable products, which as a result may be more sinterable. SHS products are typically very porous and this can be a desirable property. Examples of applications of the porous nature of SHS products include radioactive waste storage,\textsuperscript{26,27} high temperature filters,\textsuperscript{11} permeable membranes\textsuperscript{11} and catalysts.\textsuperscript{3,15,16}

SHS also has its disadvantages. The porosity associated with the SHS process is sometimes undesirable, so subsequent densification steps are required. The high reaction rates make it difficult to control the product microstructure. Industrial use of SHS is limited due to problems with scaling up the reactions and the costs attached to installing new plant. Examples do exist of companies that have made use of SHS. For instance, the Spanish company SHS Ceramicas produces Si$_3$N$_4$ by SHS.\textsuperscript{3} The London and Scandinavia Metallurgical Co. produce chromium metal by SHS via the Goldsmidt reaction (Eqn. 1.1).\textsuperscript{28} In Russia a variety of ceramic powders, pastes and products are made by the SHS route, often in large quantities ca. 100 tonnes.\textsuperscript{3}
1.3 Ferrites

1.3.1 Spinels, garnets and hexagonal ferrites

Magnetic oxides are commonly known as ferrites. This class of material includes the spinels, garnets and hexagonal ferrites. The relationship between the classes of ferrites can be seen by considering the ratio of iron oxide to metal oxide as shown in Table 1.1. They are ceramics, rather than metallic. Examples of metallic magnetic materials are Nd$_2$Fe$_{14}$B and SmCo$_5$.

Table 1.1 – Ratio of iron oxide to metal oxide for the different types of ferrites.

<table>
<thead>
<tr>
<th></th>
<th>Fe$_2$O$_3$</th>
<th>MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Garnet</td>
<td>5</td>
<td>3 Re$_2$O$_3$</td>
</tr>
<tr>
<td>Hexagonal (M-type)</td>
<td>6 Fe$_2$O$_3$</td>
<td>1 MO</td>
</tr>
</tbody>
</table>

M = transition metal, Re = rare earth metal

Spinels have the general formula AB$_2$O$_4$ and are isostructural with the naturally occurring MgAl$_2$O$_4$. They are made up of oxygen anions which form a face centred cubic structure and cations which occupy the tetrahedral (A) and octahedral (B) interstitial sites. Figure 1.3 shows a formula unit for a spinel structure; eight of these AB$_2$O$_4$ formula units make up the unit cell. There are 64 available tetrahedral sites in the unit cell of which 8 are occupied, and 32 available octahedral sites of which 16 are occupied.
Figure 1.3 – Spinel structure. One AB₂O₄ formula unit is shown – eight of these make up the unit cell. Only the front tetrahedral sites and the top face and centre octahedral sites are shown; there are effectively eight tetrahedral and four octahedral sites in this cube (from Parish²⁹).

Spinel ferrites have the general formula MFe₂O₄, where M is a divalent cation. They are soft magnetic materials and find applications in transformer cores. The -8 charge of the oxygen anions must be balanced by the M and Fe cations. A common way that this is achieved is by having a divalent cation M²⁺ and two trivalent iron cations Fe³⁺, or a trivalent cation M³⁺ with Fe²⁺ and Fe³⁺. These cations can occupy the tetrahedral and octahedral sites in different ways – this is described by the normal and inverse spinel structures.

The normal spinel structure is (M)ₐ[Fe₂]ₖ₂O₄, where the metal cation M occupies the tetrahedral A sites and the Fe cations occupy the octahedral B sites. The inverse structure is (Fe)ₐ[MFe]ₖ₂O₄, where the metal cation occupies half of the B sites, and the Fe cations occupy the remaining B sites and all of the A sites. It is also possible for spinels to have structures between the extremes of normal and inverse. To describe these structures an inversion parameter x is used. The spinel structure is then written as (M₁₋ₓFeₓ)ₐ[MₙFe₂₋ₓ]ₖ₂O₄ where an inversion parameter of x = 0 corresponds to the normal structure, and x = 1 is inverse. Whether the structure is normal or inverse depends on whether the M cations prefer to occupy
tetrahedral or octahedral sites. This in turn depends on the size of the sites and the crystal field stabilisation energy.

Garnets have the general form $\text{Re}_3\text{Fe}_5\text{O}_{12}$, where Re is a trivalent rare earth ion. They have a cubic structure and are soft magnetic materials due to their low coercivity. Yttrium iron garnet (YIG, $\text{Y}_3\text{Fe}_5\text{O}_{12}$) is a common example of a garnet ferrite. Garnets are classed as microwave ferrites; they have high resistivities which means they can operate at microwave frequencies (100 MHz to 500 GHz) without eddy current losses. They are used in microwave devices such as waveguides.$^{30,31}$

Hexagonal ferrites are a family of related compounds. The different phases that exist are shown in the ternary phase composition diagram $\text{BaO-MO-Fe}_2\text{O}_3$, where M is a divalent ion, see Figure 1.4. The letters M, U, W, X, Y and Z denote important hexagonal ferrite phases. All the ferrites are found on the lines connecting the M and S phases and M and Y phases. The different ferrites can be simplified by considering that they are made up of the following layers or blocks: S = spinel block with 2 oxygen layers, R = hexagonal block with 3 oxygen layers, and T = hexagonal block with 4 oxygen layers. Different hexagonal ferrite phases are listed in Table 1.2 with a description of their layer stacking.

The M-type hexagonal ferrite is of the form $\text{MFe}_{12}\text{O}_{19}$, where M = Ba, Sr, Ca, Pb, and is the one with the most technological interest. It is isomorphous with the naturally occurring mineral magnetoplumbite, $\text{PbFe}_{7.5}\text{Mn}_{3.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$; the magnetoplumbite structure of $\text{BaFe}_{12}\text{O}_{19}$ is shown in Figure 1.5 (a).
Figure 1.4 – Compositional diagram for BaO-MO-Fe$_2$O$_3$. The letters M, U, W, X, Y and Z denote different types of hexagonal ferrite (from Landolt-Börnstein$^{32}$). The letter F represents BaFe$_2$O$_4$ (which has a structure similar to BaAl$_2$O$_4$$^{33}$) and S represents a spinel ferrite.

Table 1.2 – Descriptions of different types of hexagonal ferrites.

<table>
<thead>
<tr>
<th>Type of hexagonal ferrite</th>
<th>Chemical formula</th>
<th>Crystallographic build-up (layer stacking)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>BaFe$<em>{12}$O$</em>{19}$</td>
<td>RSR*$S^*$</td>
</tr>
<tr>
<td>U</td>
<td>Ba$<em>2$MFe$</em>{18}$O$_{30}$</td>
<td>RSR*$S^<em>$T</em>$S^*$</td>
</tr>
<tr>
<td>W</td>
<td>BaM$<em>2$Fe$</em>{16}$O$_{27}$</td>
<td>RS$_2$R*$S^*$_2$</td>
</tr>
<tr>
<td>X</td>
<td>BaMFe$<em>{14}$O$</em>{23}$</td>
<td>3(RS$_2$R*$S^*$)</td>
</tr>
<tr>
<td>Y</td>
<td>BaMFe$<em>6$O$</em>{11}$</td>
<td>3(ST)</td>
</tr>
<tr>
<td>Z</td>
<td>Ba$<em>3$M$<em>2$Fe$</em>{24}$O$</em>{41}$</td>
<td>RSTSR*$S^<em>$T</em>$S^*$</td>
</tr>
</tbody>
</table>

Table adapted from Landolt-Börnstein$^{32}$ and Kojima.$^{34}$ $^*$ denotes a 180° rotation about the $c$ axis.

1.3.2 BaFe$_{12}$O$_{19}$

BaFe$_{12}$O$_{19}$ is an M-type hexagonal ferrite. Its crystal structure was reported by Adelsköld in 1938$^{35}$ and it was introduced with the commercial name of Ferroxdure by Philips Laboratories in 1952.$^{36}$ The structure of BaFe$_{12}$O$_{19}$ is shown in Figure 1.5 (a). It is described by the oxygen ions in alternating hexagonal and cubic spinel close packed blocks, RSR*$S^*$ (see Section 1.3.1). There are 2 formula units per unit cell. The Fe$^{3+}$ ions occupy the interstitial positions of the
oxygen lattice. There are 5 sublattices of Fe$^{3+}$ ions,$^{34}$ as described in Table 1.3. The lattice parameters of BaFe$_{12}$O$_{19}$ are $a = 5.892$ to 5.894 Å and $c = 23.183$ to 23.215 Å.$^{37,38,39}$

Figure 1.5 – (a) BaFe$_{12}$O$_{19}$ crystal structure. The unit cell is shown; it consists of two formula units (from Valenzuela$^{31}$). (b) The exchange interactions between the spins of the Fe$^{3+}$ ions in the different sites in the BaFe$_{12}$O$_{19}$ structure. This illustrates the ferrimagnetic nature of barium ferrite (from Kojima$^{34}$).
Table 1.3 – Fe$^{3+}$ sublattices in BaFe$_{12}$O$_{19}$.

<table>
<thead>
<tr>
<th>Block</th>
<th>Sublattice$^a$</th>
<th>Spin</th>
<th>Number of ions per formula unit</th>
<th>Coordination</th>
<th>Coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>2a</td>
<td>↑</td>
<td>1</td>
<td>Octahedral</td>
<td>6</td>
</tr>
<tr>
<td>S</td>
<td>4f$_4$</td>
<td>↓↓</td>
<td>2</td>
<td>Tetrahedral</td>
<td>4</td>
</tr>
<tr>
<td>S-R</td>
<td>12k</td>
<td>↑↑↑↑↑↑</td>
<td>6</td>
<td>Octahedral</td>
<td>6</td>
</tr>
<tr>
<td>R</td>
<td>2b</td>
<td>↑</td>
<td>1</td>
<td>Trigonal bipyramidal</td>
<td>5</td>
</tr>
<tr>
<td>R</td>
<td>4f$_6$</td>
<td>↓↓</td>
<td>2</td>
<td>Octahedral</td>
<td>6</td>
</tr>
</tbody>
</table>

a – Wyckoff$^a$’s notation

Barium ferrite is a permanent magnetic material. It has a saturation magnetisation, $\sigma_s$, of 67-72 emu g$^{-1}$ at room temperature.$^{34}$ Its magnetism is due to the ordering of the spins of the Fe$^{3+}$ ions. It has ferrimagnetic order, which means that the spins are oriented opposite to one another but in unequal numbers, so there is a net magnetic moment. The reason the spins line up relative to each other is due to an exchange interaction. In ferrimagnetic and antiferromagnetic ordering the exchange interaction is negative, whereas in ferromagnetic ordering the exchange is positive. Raising the temperature disturbs the magnetic ordering. Barium ferrite has a Curie temperature of 450 °C$^{32}$ above which it is paramagnetic.

The spins of the Fe$^{3+}$ ions in BaFe$_{12}$O$_{19}$ do not interact directly. Instead they interact through the oxygen ions – this is known as superexchange. The interactions between the spins on the Fe$^{3+}$ ions in the different sublattices is shown in Figure 1.5 (b). The largest interaction energy is between the Fe$^{3+}$ ions in the 2b and 4f$_6$ sites$^{34}$ where the Fe-O-Fe bond angle is closest to 180°, so this contributes most to the magnetic order of barium ferrite.

Barium ferrite is a hard magnetic material, due to its high coercivity (ca. 2000-5000 Oe)$^{32,40}$ This means that it is difficult to demagnetise, which makes it useful as a permanent magnet. Coercivity, $H_c$, is the field that must be applied to demagnetise a material from magnetic saturation; coercive field is the field that is
applied from an arbitrary magnetisation. Hard magnetic materials are those with
$H_c > 125$ Oe; soft magnetic materials have $H_c < 12.5$ Oe.$^{30}$

The intrinsic coercivity of barium ferrite is due to its magnetocrystalline
anisotropy, although other factors such as particle shape, microstructure and
imperfections can act to alter the observed coercivity. Anisotropy is where there
are certain preferred directions, or easy axes, for the magnetisation and these
lower the total energy of the crystal. Magnetocrystalline anisotropy is an intrinsic
property of the material. It has a magnetostatic contribution from dipole
interactions between ions (2-ion anisotropy), and a magnetoelectric contribution
from the interaction between an ion and the crystal field (single-ion anisotropy).$^{41}$

The other main type of anisotropy is shape anisotropy, which is macroscopic and
due to interactions between magnetic dipoles. It is restricted to small particles
($< \mu \text{m}$) and is not considered for barium ferrite. The large crystalline anisotropy of
barium ferrite is mainly due to the single ion anisotropy of Fe$^{3+}$ at the 2b and 4f$_e$
sites.$^{42}$

The anisotropy in barium ferrite is uniaxial, which means there is one easy axis.
The easy axis is along the $c$ axis in the hexagonal crystal structure. This can be
seen in Figure 1.5 where the spins are aligned either parallel or anti-parallel to the
$c$ axis.

To modify the coercivity of barium ferrite its crystalline anisotropy must be
altered. This can be done by doping other ions into the structure to replace Fe$^{3+}$
ions, especially on the 2b and 4f$_e$ sites. Substitution of Co$^{2+}$ and Ti$^{4+}$ is
popular$^{24,43,44}$ because these ions reduce the coercivity without significantly
affecting the saturation magnetisation. These substitutions work because Co$^{2+}$ and
Ti$^{4+}$ are non-magnetic ions, so some of the magnetic exchange interactions are
destroyed. Since Fe$^{3+}$ ions in the 4f$_e$ and 2b sites provide the largest contributions
to the anisotropy, replacing ions on these sites in particular leads to a decrease in
the anisotropy. Doping can also affect the magnetisation. With reference to Figure
1.5 (b), substituting for spin-up Fe$^{3+}$ reduces the net magnetisation, while
substituting for spin-down Fe$^{3+}$ increases it.

Barium ferrite has a wide range of applications, which include permanent
magnets\textsuperscript{20} used in loudspeakers, motors,\textsuperscript{45} magnetic levitation and toys;\textsuperscript{46} and
magnetic recording on credit/debit cards,\textsuperscript{47} magnetic tape, floppy disks\textsuperscript{42} and
magneto-optic recording media.\textsuperscript{43} More unusual applications include its use as a
catalyst, and in medical equipment.\textsuperscript{46}

1.4 Reactions in magnetic fields

Magnetic fields have been reported to affect a number of different chemical
reactions, in the gas phase, liquid phase and solid phase.

1.4.1 Effect of magnetic fields on gas phase reactions

Inhomogeneous magnetic fields have been reported to promote combustion in
diffusion flames.\textsuperscript{48} The influence of magnetic fields on flames was studied in the
1840s by Michael Faraday.\textsuperscript{49} He found that a flame on a wax taper tended to be
deflected towards lower field strengths. Recently experiments have been
performed with a fuel gas (e.g. methane) flowing between the poles of an
electromagnet, to create a flame at different positions relative to the field, as
shown in Figure 1.6. At position A, with the fuel gas flowing towards decreasing
field strength, the flame became sharper, brighter and hotter. When the flame was
in a region of zero field gradient, position B, no effect was observed on the flame.
At position C, the flame was deflected into a disk shape. (Faraday conducted his
experiments in an arrangement equivalent to position C.) Photographs of the
flames in zero field and in a gradient magnetic field of 0.35 T cm\textsuperscript{-1} (at position A)
are shown in Figure 1.7.
Figure 1.6 – Diagram of experiments on diffusion flames in different positions relative to a gradient magnetic field (from Wakayama and Sugie\textsuperscript{48}).

Figure 1.7 – Photographs of flames with fuel gas flowing towards decreasing field strength (at position A): (a) flame in zero field, (b) flame in gradient magnetic field of 0.35 T cm\textsuperscript{−1} (from Wakayama and Sugie\textsuperscript{48}).

The effect of a field gradient on a flame was explained by paramagnetic oxygen gas being attracted in the direction of increasing magnetic field strength. This was the case for flames in position A. The magnetic attractive force therefore increases the oxygen supply to the combustion process. Convection is also enhanced. The magnetic force per unit volume, $F$, is given in Eqn. 1.6 (from Wakayama and Sugie\textsuperscript{48}).
where $p_o$ is the partial pressure of oxygen gas, $\chi_o$ is the magnetic susceptibility of oxygen and $H$ is the magnetic field strength. The authors calculated the magnetic force on oxygen in 1 cm$^3$ of air to be about $1.5 \times 10^{-5}$ N, in a one dimensional magnetic field gradient of 0.5 T cm$^{-1}$. This magnetic force can be compared with the force due to gravity acting on the oxygen present in 1 cm$^3$ of air. Using the ideal gas law, $PV = nRT$, 1 cm$^3$ of air is calculated to contain $2.4 \times 10^{19}$ atoms. Taking into account that only $\sim 20\%$ of the volume of air is oxygen means that 1 cm$^3$ of air contains $\sim 5 \times 10^{18}$ oxygen atoms. From Newton’s second law, $F = ma$, the force due to gravity on the oxygen atoms in 1 cm$^3$ of air is calculated to be $\sim 1.3 \times 10^{-6}$ N. This is an order of magnitude smaller than the magnetic force on oxygen in the same volume of air.

Diffusion flames are those where the oxygen is supplied to the flame by diffusion from the surrounding air. Experiments on premixed flames, where the oxygen is mixed with the fuel, showed that they are not influenced by magnetic field gradients. Further evidence that the promotion of combustion is due to the attractive force on oxygen, is supplied by combustion experiments under microgravity. In micro-gravity, natural convection does not exist and flames are quickly extinguished. By applying a magnetic field gradient, flames lasted much longer, which was explained by the attraction of oxygen into the increasing field.

Another example of a gas phase reaction which is influenced by magnetic fields is the arc discharge synthesis of carbon nanotubes and fullerenes. Magnetic fields up to 10 T were applied during discharge. Application of a magnetic field was found to produce nanotubes of a different morphology to normal, and it affected the ratio of C$_{70}$ to C$_{60}$ obtained. These effects were explained in terms of the magnetic field affecting the arc discharge.
1.4.2 Effect of magnetic fields on liquid phase reactions

Magnetic fields have been reported to affect the electrodeposition of copper from copper sulphate solution. Changes in the shape and chirality of the copper deposits were observed, as shown in Figure 1.8. A uniform magnetic field applied perpendicular to the reaction cell gave a branched, spiral pattern. Reversing the direction of the field reversed the chirality of the spiral. When the field was applied parallel to the plane of the cell, a stringy deposit perpendicular to the field direction was generated. The diffusion coefficient doubled in a field of 1 T compared to zero field, and the fractal dimension of the deposits increased with perpendicular field strength. The authors said that the direct effect of the Lorentz force was too small to account for these effects, although it helped to explain the chirality and shape of the deposits. Instead, the field was thought to modify the ion transport rate on a scale of a few microns near the cathode, where the magnetic force on the ions is comparable to the gravitational force.\footnote{52,53}

![Image of electrodeposits of copper in different conditions]

Figure 1.8 – Electrodeposits of copper in different conditions: (a) zero field, (b) 0.4 T upwards, (c) 0.8 T downwards, (d) 1 T horizontally in plane of cell in the direction of the arrow (from Coey et al.\footnote{52}).

42
Another example of the influence of magnetic fields on liquid phase reactions is for a process called magnetic melt processing, where textured crystals are grown in magnetic fields. A field of 9 T was used to produce texture, or preferential orientation of crystals, in Bi(Pb)2212.\textsuperscript{54} (Bi(2212) is a high-\(T_c\) superconductor with the formula \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}\); in Bi(Pb)2212 it has been doped with lead.) The sample melted and crystallised during synthesis. Significant preferential orientation was observed for the sample synthesised in the magnetic field; the \((0\ 0\ 1)\) reflection lines were enhanced, indicating grains with their \(c\) axes parallel to the field.

1.4.3 \textit{Effect of magnetic fields on solid phase reactions}

Very little work has been done on studying the effect of magnetic fields on SHS reactions, and to the best of our knowledge, magnetic fields have not been reported to influence other types of solid state reactions. The effect of magnetic fields on SHS reactions is discussed below, Section 1.5.

1.5 \textit{SHS in magnetic fields}

The first report of the application of a magnetic field on SHS was in 1986 for reactions of the ferromagnetic metals Fe, Co or Ni with either S or Al, and some non-ferromagnetic metals Ti, Mo, Cr, Mn and Cu with S.\textsuperscript{55} Different ferrite\textsuperscript{56,57,58} and intermetallic\textsuperscript{59} systems have since been studied at field strengths up to 1.9 T. Some of this work on the influence of magnetic fields on SHS has appeared during the course of this project. Conducting SHS reactions on powders in magnetic fields was observed to increase the combustion temperature and the wave velocity. The field led to a faster cooling rate of the product and a higher degree of conversion to the product phase. Products synthesised in a magnetic field were found to have increased magnetisations and reduced coercivities. Magnetic fields were also found to increase the magnitude and duration of the combustion electromotive force (e.m.f.). (The combustion e.m.f. is an electrical signal generated by the SHS wave and is described further in Section 1.6.)

Significantly, magnetic fields were only found to affect the combustion parameters of systems containing ferromagnetic components.\textsuperscript{55} The orientation of
the field relative to the direction of wave propagation was also an important factor.

Komarov et al. synthesised SrFe\textsubscript{12}O\textsubscript{19} in a 0.3 T magnetic field (in 1994).\textsuperscript{56} Magnetic field synthesis on the powdered green mixture led to an increase in the combustion temperature of 150 °C and a seven-fold increase in the velocity. The saturation and spontaneous magnetisation of the product increased, while its coercivity decreased from ~2000 Oe to ~200 Oe for the applied field product. The degree of conversion also increased, i.e. more ferrite phase was formed, and the macrostructure of the product was anisotropic – chains of Sr\textsubscript{7}Fe\textsubscript{10}O\textsubscript{22} coincided with the field direction, with SrFe\textsubscript{12}O\textsubscript{19}, SrO and Fe\textsubscript{2}O\textsubscript{3} in between the chains.

Morozov and Kuznetsov synthesised LiFe\textsubscript{2} in magnetic field strengths up to 0.27 T (in 1999).\textsuperscript{57} The experiment set-up is shown in Figure 1.9. (The green mixture was in powder form.) Magnetic field synthesis led to a 30 % increase in the combustion velocity compared to zero field. The magnitude and duration of the combustion e.m.f. increased with magnetic field strength. In this experiment the wave could travel either parallel or perpendicular to the magnetic field. This resulted in an anisotropy of the combustion e.m.f. response; the results are discussed further in Section 1.5.4.

![Diagram](image)

**Figure 1.9** - Experiment set-up for SHS reactions in a magnetic field of 0.27 T (from Morozov and Kuznetsov\textsuperscript{57}).
Morozov synthesised $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ and $\text{LiFeO}_2$ in a 0.01 T or 0.3 T magnetic field (in 1999).\(^5\) (The green mixture was in powder form.) The field affected the phase composition, with the amount of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ as a second phase in $\text{LiFeO}_2$ increasing with field strength. The magnetisation of both of the products was larger for those made in a magnetic field compared to zero field. For example, for $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ the magnetisation increased by $\sim 100\%$ in 0.3 T vs. zero field. The magnetisation also depended on the orientation of the field relative to the wave. When the magnetic field was parallel to the propagation direction it led to greater magnetisations ($\sim 40\%$ larger) compared to the perpendicular orientation.

1.5.1 Effect of magnetic fields on pellet reactions

Pressed pellets of green mixture have also been studied by Kirdyashkin et al. (in 1999)\(^6\) to compare with the results from experiments on powders. In pressed pellets the ferromagnetic components were assumed to be unable to align with the magnetic field. Reactions were performed on different intermetallic systems, Ni-Al, Co-S, Ti-FeB and Ti-C in magnetic fields of up to 1.9 T. Notably the magnetic field was aligned perpendicular to the direction of wave propagation. The authors report that a constant transverse magnetic field does not affect the reaction velocity. However, they did not try using a constant longitudinal (parallel) field, which for powders had been seen to alter the reaction velocity. For the systems containing ferromagnetic components, the transverse magnetic field led to the reaction going further to completion. X-ray microanalysis scans of the products showed that those synthesised in the magnetic field contained a smaller fraction of the starting materials compared to the zero field products. Also, magnetic field synthesis led to larger regions of each phase in the product structure, as shown in Figure 1.10 and Figure 1.11.
Figure 1.10 – Nickel distribution in Ni-Al SHS product synthesised from a pellet in (a) zero field, (b) magnetic field of 1.9 T (from Kirdyashkin et al.59). (The direction of the field relative to these sections is unclear).

Figure 1.11 – Volume fraction vs. size of Ni$_2$Al$_3$ regions for SHS product synthesised from a pellet in (a) zero field and (b) magnetic field of 1.9 T (from Kirdyashkin et al.59).

1.5.2 Explanations of magnetic field effects

Some authors attribute the influence of a magnetic field on iron-based powder to the iron particles agglomerating to form chains aligning with the magnetic field lines.56,57,58 This is said to increase the effective thermal conductivity.55 However, agglomeration of iron particles cannot be used to explain the influence of
magnetic fields on pellets, because the particles are probably unable to move. Some movement of the particles may still be possible in a pellet, although their movement will have been hindered considerably by pelletizing.

Instead of agglomeration, Kirdyashkin et al. explain the effect of the magnetic field on pellets by saying it improves mass transport in the reaction products behind the SHS wave. They proposed that the field acts by the phenomenon of magnetophoresis, which is the movement of charged particles in a fluid under the influence of a magnetic field. (Phoresis is Greek for "being carried"). The liquid and solid phases separate due to a pressure difference at the phase boundaries, which is related to the difference in the magnetisations of each phase. It causes something similar to a buoyancy force in the presence of an inhomogeneous magnetic field. The mass transport by diffusion increases because the liquid and solid phases are both moving. The solid parts tend to merge together in the region behind the propagation wave. The size of the magnetophoresis effect is proportional to the difference between the magnetisations of the two phases. If both phases are only weakly magnetic then the effect of the field will be weak.

1.5.3 Relation of magnitude of field effect with Curie and combustion temperature

Magnetic fields have only been reported to act on ferromagnetic or ferrimagnetic components. A ferromagnet is only magnetic below its Curie temperature; above that it becomes paramagnetic. SHS reactions generate high temperatures. Ferromagnetic reactants and products will lose their strong magnetic response if the combustion temperature exceeds their Curie temperatures. A magnetic field will influence the reaction most strongly when the material is ferro- or ferrimagnetic, i.e. when the temperature falls below the Curie temperature of the reactants and/or products. It follows that the magnetic field will have most influence for reactions where the combustion temperature is below the Curie temperatures of any of the reactants or products involved.

An example is the reaction to form Li$_{0.5}$Fe$_{2.5}$O$_4$. It has a combustion temperature of 850 K (as stated by the authors, although very low for an SHS reaction) which
is less than the Curie temperatures of the reactants or products. The magnetic field therefore has a strong influence throughout the reaction, during the heating, melting, reaction and cooling phases. By contrast, the reaction to form LiFeO$_2$ has a higher combustion temperature of 1260 K which is greater than the Curie temperature of Fe (1043 K) and LiFeO$_2$ (943 K). In this case, the field acts most strongly during the heating and cooling stages, and only has a weak influence above the Curie temperature.

### 1.5.4 Direction of wave relative to magnetic field direction

The direction of the magnetic field relative to the direction of the SHS propagation wave is an important consideration that has been investigated in the literature$^{56,57,58,59}$ for fields either parallel or perpendicular to the propagation direction. Additionally, the wave may travel from the north (N) to the south (S) pole of the magnet, or *vice versa*, depending on the end at which it is initiated. Reactions may be performed on either powders or pellets. With pellets, the field may either be in the plane of the pellet or perpendicular to the pellet’s surface. It seems reasonable that magnetic fields parallel to the direction of SHS propagation should affect the reaction (see Section 1.5.2), although fields perpendicular to the wave direction may also have an influence.

An example of the influence of magnetic field direction on a powder reaction is the synthesis of LiFeO$_2$ with the propagation wave parallel and perpendicular to the magnetic field of 0.3 T.$^{57,58}$ The magnetisation of the product synthesised in a parallel field was ~40 % larger than the product from a perpendicular field.$^{58}$ However, it is not clear whether the perpendicular field had an effect on the reaction compared to zero field. In the parallel arrangement, the reaction could be ignited at either the N or S pole of the magnet,$^{57}$ and in the perpendicular arrangement, the reaction could be ignited at either of the exposed ends, as shown in Figure 1.12. Changing the direction of the wave relative to the field resulted in an anisotropy of the combustion e.m.f. response, i.e. the responses were not identical. The sign of the e.m.f. was reversed for the parallel orientation, but not for the perpendicular case.
Figure 1.12 - Combustion e.m.f. signals generated by SHS reactions (Li$_2$O$_2$ + Fe + 0.5 Fe$_2$O$_3$ → 2 LiFeO$_2$) in a magnetic field of 0.23 T, with the wave propagating in different directions relative to the field, as illustrated (from Morozov and Kuznetsov$^{57}$).

For reactions on pellets, a magnetic field of up to 1.9 T perpendicular to the wave caused no change in the reaction velocity compared to zero field.$^{59}$ This should be contrasted with reactions on powders parallel to the field, where the field has a significant influence on the velocity.$^{56}$ It should be noted that for pellets, no experiments were reported for the wave parallel to the field direction.$^{59}$ It would be interesting to learn if a parallel field affects pellets as well as loose powders, and if a perpendicular field affects powders as well as pellets.
1.6 Generation of electric and magnetic fields by SHS

In the previous section it was shown that an externally applied magnetic field affects SHS reactions. In this section we will see that magnetic and electric fields are generated by the passage of an SHS propagation wave. Magnetic fields are created by moving charges and electric fields exist when there are more charges in one place compared to another. The existence of magnetic and electric fields at the wavefront may help to explain the influence that externally applied magnetic fields have on SHS reactions.

"Chemomagnetism" describes the generation of a magnetic field by a chemical reaction. The phenomenon of chemomagnetism was observed for SHS reactions on various green mixtures. Two different groups of SHS reactions were studied: one group was made up of non-ferromagnetic reactants, to produce non-ferromagnetic oxides, whereas the other group had ferromagnetic oxide products. A high-Tc SQUID magnetometer was used to measure the very weak (~nT) magnetic fields generated by these reactions; the experimental set-up used is shown in Figure 1.13.

In the synthesis of non-ferromagnetic oxides, a rapidly oscillating magnetic field was produced which decayed to zero, Figure 1.14 (a) and (b). In the synthesis of ferromagnetic oxides, a permanent magnetic field was generated, Figure 1.14 (c) and (d). If the combustion temperature exceeded the Curie temperature, the measured magnetic field initially decreased until the temperature went below the Curie temperature, when the field began to increase to its final value, Figure 1.14 (c). If the combustion temperature did not exceed the Curie temperature, the magnetic field increased monotonically to its final value, Figure 1.14 (d). This relates to the work described in Section 1.5.3, where the size of the effect of the magnetic field was found to be dependent on the relationship between the combustion temperature and the Curie temperature.
Figure 1.13 – Experimental set-up to measure magnetic fields generated by SHS reactions (from Nersesyan et al.).

(a) Quartz tube containing green mixture
(b) Thermally isolated enclosure
(c) Match
(d) High-Tc SQUID magnetometer
(e) Fibreglass liquid nitrogen dewar
(f) Cryogenic cable to transmit SQUID signal
(g) High-permeability shielding to eliminate background noise

Figure 1.14 – Magnetic signals generated by SHS reactions. The reactants and products in (a) and (b) are non-ferromagnetic whereas in (c) and (d) they are ferromagnetic. (a) SrO₂ + 0.4 Ti + 0.6 TiO₂ → SrTiO₃, (b) Ti + 5.5 TiO₂ + 0.5 NaClO₄ → TiO₂ + 0.5 NaCl, (c) 0.5 Na₂O₂ + Fe → 4 NaFeO₂, (d) 2 Na₂O₂ + Fe + 1.5 Fe₂O₃ → 4 NaFeO₂ (from Nersesyan et al.).
The generation of magnetic fields can be explained by discussing "chemoionisation" processes. Chemoionisation is "chemical rearrangement which releases energy and leads to ionisation of the products".\textsuperscript{62} Ions are produced in and around the combustion wave region during the formation of complex oxides, by decomposition of the peroxide reactant, oxidation of the fuel, and by reactions in the post-combustion zone. Transient local excesses of cations and anions, their relative motions, and velocity fluctuations of the combustion wave could all explain the oscillations observed in the induced magnetic field.

Electric fields are also generated by the passage of an SHS wave,\textsuperscript{57,61,63} referred to earlier as the combustion e.m.f. A variety of SHS reactions were studied, by measuring the potential difference between two electrodes a fixed distance apart, as shown in Figure 1.9. Patterns of positive and negative peaks were measured, shown in Figure 1.12. The potential difference arises due to different amounts of charge between the reacted product at one electrode and the SHS wavefront at the other electrode. Chemoionisation processes again explain these effects. A current of anions gives a negative peak, whereas cations give a positive peak. Stronger signals were observed for reactions requiring oxygen and those with more complex products.

1.7 Previous work by the UCL group

The UCL group first reported work on SHS in 1997, for the synthesis of barium and strontium hexagonal ferrites.\textsuperscript{64,65,66,67} In these publications, SHS was described as a new route to strontium and barium ferrite. The reactions were performed in air and oxygen and the effect of varying the component ratios was studied. At that time all the reactions were performed in zero field. Then, in 1998, the first work was published of SHS reactions in a 1.1 T magnetic field\textsuperscript{68,69,70,71,72} for the synthesis of pure and chromium-doped barium ferrite, lithium ferrite and magnesium-zinc ferrite.
The magnetic field produced a number of effects, the precise nature of which depended on the system in question. For the synthesis of BaFe$_{12}$O$_{19}$ the magnetic field was observed to result in a needle-like microstructure in the post-SHS product, which was not seen in the zero field product. The coercive field of the annealed BaFe$_{12}$O$_{19}$ product made in the magnetic field was found to be ~20% lower than the zero field product (1800 Oe vs. 2400 Oe). For the synthesis of Li$_{0.5}$Fe$_{2.5}$O$_{4}$ the magnetic field resulted in a reduction in coercive field (18.4 to 14.5 Oe), and an increase in maximum magnetisation (51.6 to 54.7 emu g$^{-1}$) of the product compared to the zero field product. Also, an increase in the amount of superstructure was noted, from 30% in zero field to 87% in the 1.1 T product. The applied field synthesis of Mg$_{0.5}$Zn$_{0.5}$Fe$_{2}$O$_{4}$ showed a large (~35%) increase in the maximum magnetisation of the product (60 to 83emu g$^{-1}$) and a slight decrease in the lattice parameter. For all of the systems, the magnetic field led to a hotter and faster reaction than in zero field.

Some explanations for the effects of the magnetic field were proposed. Pre-organisation of the green mixture in the field was one such suggestion, leading to better particle contact and hence hotter and faster reactions. A related idea was that magnetic components could be drawn into the reaction zone by the magnetic field. The differences in the products due to the field could not be explained by changes in occupancy of the lattice sites. Instead, changes in magnetic microstructure were said to be responsible.

1.8 Overview

Self propagating high temperature synthesis or SHS describes highly exothermic solid state reactions that proceed via a propagation or combustion wave. Familiar examples include the Goldsmidt reaction to produce chromium by SHS, and the Thermite reaction which is used in welding. SHS has only been studied as a scientific field since the late 1960s after its discovery by Russian researchers in Chernogolovka.
There are various ways to categorise SHS reactions, in terms of the modes of propagation, the physical state of the reactants (homogeneous or heterogeneous systems), and the combustion mechanism (equilibrium or non-equilibrium). Important parameters for characterising SHS reactions include the ignition temperature, the adiabatic combustion temperature and the reaction velocity. The conditions that describe whether or not a particular reaction will undergo SHS have been determined from both experiment and theory – it depends on the exothermicity of the reaction, the ignition temperature, adiabatic combustion temperature, and the heat capacities of the reactants and the products.

SHS is a type of solid state reaction. Solid state reactions are slow because the solid state diffusion barrier must be overcome for neighbouring particles to react. The standard ceramic processing route involves heating the starting materials to high temperatures. Synthetic methods such as chemical co-precipitation and glass crystallisation attempt to overcome the problems with the ceramic processing route, although they are quite chemically involved. SHS has many advantages compared to these synthetic routes, such as its speed, simplicity and low cost, as well as the potential to form metastable products. Disadvantages of SHS include the porous nature of the products and difficulties in controlling the product microstructure.

Ferrites are magnetic oxides and are used in transformer cores, microwave devices, loudspeakers and motors. Spinel, garnet and hexagonal ferrites have different crystal structures and magnetic properties. The structure and properties of the hexagonal M-type ferrite BaFe$_{12}$O$_{19}$ have been described in this chapter.

Magnetic fields have been reported to affect a number of different chemical reactions in the gas phase, liquid phase and solid phase. Examples include experiments on diffusion flames and on electrodeposition in the presence of a magnetic field. Different explanations for these effects were proposed, such as paramagnetic oxygen being attracted into the magnetic field, or the field influencing ions, perhaps by the Lorentz force. Some experiments on the influence
of magnetic fields on SHS reactions have also been reported. Effects observed included higher reaction temperatures and velocities, a greater degree of conversion to the desired product phase and changed magnetic properties. Magnetic fields were only found to affect reactions on systems containing ferromagnetic components. Issues addressed included whether the reaction was on a powder or a pellet, the direction of the propagation wave relative to the magnetic field direction and the relationship between the Curie temperature and the combustion temperature. Explanations for the field effects were the formation of chains of ferromagnetic particles along the field direction, and magnetophoresis – the separation of liquid and solid phases due to the action of the magnetic field, improving the mass transport. The generation of electric and magnetic fields by SHS reactions has also been discussed in this chapter.

Previous work by the UCL group on the SHS of ferrites has been reviewed. This included reactions in a magnetic field.

The aim of this project is to investigate how applied magnetic fields influence SHS reactions to form ferrites. The goal was to be able to control the microstructure and magnetic properties of the product by controlling the reaction conditions. In particular, could synthesis in a magnetic field be used to change the magnetic properties of the ferrite products? The aim has been to explore what happens and why it happens. To understand the influence of the magnetic field, the influence of other processing parameters such as particle size and oxygen source and flow rate had to be understood. This built on previous experiments by the UCL group on the SHS of ferrites in a magnetic field. To aid our understanding of the influence of the field, the reactions were studied in situ by time resolved X-ray diffraction – a new direction for our work.

The details of the experimental work are described in Chapter 2. It includes how the green mixtures were made, how the SHS reactions were performed, and the in situ analysis of the reactions and characterisation of the products formed. The following three chapters cover the results from various experiments.
Investigations into the influence of different processing parameters on the SHS reaction and products are described in Chapter 3. Studies of the effect of a magnetic field on the SHS reaction to form BaFe$_{12}$O$_{19}$ are given in Chapter 4. In situ analysis of the reactions by time-resolved X-ray diffraction is described in Chapter 5. The conclusions are given in Chapter 6.
2 Experimental

In this chapter the experiments that were performed are described. Explanations of how the green mixtures were made, how the SHS reactions were carried out, and how the reactions and the products were analysed are given. Although the bulk of the analysis performed was on the products formed by SHS, valuable information was also obtained by analysing the reactions themselves, *in situ*.

2.1 General experimental

All the reagents were obtained from Aldrich Chemical Company and used as supplied. The particle size and chemical purity of each reagent is given in Table 2.1. Sodium perchlorate, NaClO₄, was not assayed for particle size. The powders were weighed and mixed together under a nitrogen atmosphere, inside a Saffron Scientific glove box. A nitrogen atmosphere was used because Fe is oxidised over a long period of time in air, and because BaO₂ is toxic.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Particle size / μm</th>
<th>Chemical purity / %</th>
<th>Aldrich catalogue number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>&lt;10</td>
<td>99.9+</td>
<td>26,795-3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>&lt;5</td>
<td>99+</td>
<td>31,005-0</td>
</tr>
<tr>
<td>BaO₂</td>
<td>44</td>
<td>95</td>
<td>30,912-5</td>
</tr>
<tr>
<td>NaClO₄</td>
<td>-</td>
<td>98</td>
<td>20,842-6</td>
</tr>
</tbody>
</table>

A pestle and mortar was used to grind the reagents together. The green mixtures were made on a scale of a few grams. The term "green mixture" describes the mixture of powder reagents on which SHS is performed.

Reactions were initiated by a match or hot filament and proceeded *via* a propagation wave. A photograph of an SHS propagation wave is shown in Figure 2.1. The reactions were analysed *in situ* by optical pyrometry, thermal imaging camera, video recording and time-resolved X-ray diffraction. The products were obtained in essentially quantitative yields. A portion of each product was annealed to complete the reaction. Both the post-SHS and annealed portions of the products
were characterised by some or all of the following techniques: X-ray diffraction, vibrating sample magnetometry, Mössbauer spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis, electron microprobe analysis, differential thermal analysis and thermal gravimetric analysis.

Figure 2.1 – An SHS propagation wave in zero field, for the reaction of a powder mixture of BaO₂ + Fe + Fe₂O₃ under a flow of oxygen. The strip of powder is ~8 cm long. The reaction proceeds from right to left. Photographs were taken at t = 5 s (bottom), t = 20 s (middle) and t = 35 s (top).

The driving force for the reactions is the oxidation of iron metal. Iron (III) oxide is included to act as a moderator; without it, the reaction would be much more exothermic and material could be released up to 1 m from the reaction site. Oxygen is an essential component in these reactions, and is the limiting reagent. It can come from the air, an oxygen flow, or from the reactants themselves. The metal peroxide (BaO₂) provides oxygen when it decomposes. An oxidising agent such as sodium perchlorate (NaClO₄) may also be used as an additional internal source of oxygen.

From point initiation, the reaction proceeds with a propagation wave. The product is formed in the region behind the wave and is called the post-SHS product. It is
obtained in nearly 100 % yield, with the only losses being mechanical in nature. For the purposes of further analysis, the post-SHS product was crushed with a pestle and mortar. If sodium perchlorate was used, a further washing step was required to remove NaCl that is produced during SHS. Washings were performed by suction filtration using 2 x 100 ml distilled water.

A portion of each of the post-SHS products was annealed, in order to complete the reaction. The barium ferrite post-SHS product was placed in a ceramic boat and annealed in a Carbolite rapid heating furnace at either 1150 °C for 6 hours or 1200 °C for 2 hours. The heating rate was 50 °C min⁻¹. After the annealing period the products were left in the furnace to cool overnight. The annealed product was nearly single phase BaFe₁₂O₁₉.

2.2 Green mixture preparations

2.2.1 Preparation of BaFe₁₂O₁₉ green mixture

\[
\text{BaO}_2 (1.4 \, \text{g}, \, 8.2 \, \text{mmol}), \, \text{Fe} (2.5 \, \text{g}, \, 44.8 \, \text{mmol}) \text{ and } \text{Fe}_2\text{O}_3 (3.57 \, \text{g}, \, 22.4 \, \text{mmol}) \text{ were ground together with a pestle and mortar, according to Eqn. 2.1. A 10 } \%
\]

excess of BaO₂ was used in order to produce the required barium ferrite phase, because some barium is lost as BaO when BaO₂ decomposes. The oxygen for these reactions came either from the air or from an oxygen gas supply. The products were obtained in essentially quantitative yields and were analysed by some or all of the following techniques: X-ray diffraction, vibrating sample magnetometry, Mössbauer spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis, electron microprobe analysis, differential thermal analysis and thermal gravimetric analysis.
2.2.2 Preparation of BaFe\textsubscript{12}O\textsubscript{19} green mixture with sodium perchlorate

\[ 1.1 \text{BaO}_2 + 6 \text{Fe} + 3 \text{Fe}_2\text{O}_3 + 2 \text{NaClO}_4 \xrightarrow{\text{SHS}} a \text{Fe}_3\text{O}_4 + b \text{Fe}_{1-x}\text{O} + c \text{BaFe}_2\text{O}_4 + 2 \text{NaCl} \xrightarrow{\text{wash and anneal}} \text{BaFe}_{12}\text{O}_{19} \]

BaO\textsubscript{2} (0.77 g, 4.5 mmol), Fe (1.37 g, 24.5 mmol), Fe\textsubscript{2}O\textsubscript{3} (1.97 g, 12.3 mmol) and NaClO\textsubscript{4} (1.0 g, 8.2 mmol) were ground together with a pestle and mortar, according to Eqn. 2.2. A 10% excess of BaO\textsubscript{2} was used. Sodium perchlorate (NaClO\textsubscript{4}) was ground in lightly after the other reagents had been mixed together. There was a risk of initiation because sodium perchlorate is a very strong oxidising agent. The products were obtained in essentially quantitative yields and were analysed by some or all of the following techniques: X-ray diffraction, vibrating sample magnetometry, Mössbauer spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis, electron microprobe analysis, differential thermal analysis and thermal gravimetric analysis.

2.3 Performing SHS reactions

2.3.1 Reactions in zero field

To perform the SHS reactions, the green mixture was supported on a ceramic mat or in a quartz tube. The support medium must be resistant to the high temperatures evolved in the reactions. For reactions in zero field, Figure 2.1 and Figure 2.2, the green mixture powder was laid out in a strip formation, about 1 cm wide and high and 5 cm long. The powder was ignited at one end and proceeded with a yellow-orange propagation wave of velocity \( \text{ca.} 1 \text{ mm s}^{-1} \). The propagation wave travelled along the length of the green mixture in a surface layer. It also travelled down from the surface into the bulk of the material, at a slower rate, which was observed as a broad glow. The powder darkened to brown after the wave had passed and was slightly fused.
2.3.2 Reactions in magnetic fields

SHS reactions may be conducted in an external magnetic field. A Magnetic Solutions permanent magnet Halbach cylinder, comprising eight NdFeB magnets, provided a uniform magnetic field of 1.1 T perpendicular to the cylinder axis. The magnetic field is uniform to better than ± 0.4 %. Reactions were conducted inside a quartz tube, outer diameter 18 mm, which was placed inside the 20 mm diameter bore of the magnet. The field axis was vertical (although it could be rotated to be horizontal). The experiment set-up is shown in Figure 2.3.

Figure 2.3 – Applied magnetic field 1.1 T SHS experiment set-up.

Another set-up was to use two small (25 mm diameter) NdFeB magnets placed in a special aluminium holder, with space for the quartz tube to fit between the magnets. The field supplied by this arrangement was 0.2 T in the horizontal direction, and may be referred to as the “weak field” arrangement. See Figure 2.4.
In these applied field reactions, the green mixture aligned along the direction of the magnetic field, and took up something like an hourglass shape in cross-section. The depth of the powder along the tube depended on the amount used, but was generally about 1 cm. The powder was ignited by placing a match or hot wire down one end of the quartz tube. The reaction proceeded with a yellow-orange propagation wave of velocity ca. 0.3 mm s\(^{-1}\). The product was removed from the magnetic field by inserting a plunger to force it out. The product was fused in the hourglass shape. It contained shiny, fibrous parts in the central region, as well as matt, brown coloured parts near the edges.

2.3.3 Green mixture compaction

The green mixture was normally in the form of a loose powder. However, some experiments were performed on compacts of green mixture. Compacts were made either by pressing ~1 g of the green mixture into a circular pellet, 13 or 16 mm diameter and about 1 mm thick, using a KBr die with a pressure of ~75 or ~50 MPa respectively; or by using a specially made die to press a rectangular bar (dimensions 20 x 5 x 3 mm\(^3\), ~100 MPa pressure). Reactions on pellets and bars were performed inside the quartz tube. Two short quartz tube inserts were used to keep the pellets upright, a requirement for the time-resolved X-ray diffraction work. See Figure 2.5.
2.3.4 Oxygen flow

For reactions in oxygen, a gas flow was supplied via a nozzle at one end of the tube. The flow rate was measured with a Platon oxygen flowmeter (maximum measurable rate of 12 l min$^{-1}$). The direction of the oxygen flow was opposite to the propagation direction of the SHS wave, because it was easier to ignite the mixture from one end and have the oxygen coming in from the other end, rather than having both the ignition and oxygen source at the same end of the sample. However, for the in situ analysis of the reactions by time-resolved X-ray diffraction, the oxygen was supplied at the same end as the ignition, and the incoming X-rays, to avoid obstructing the diffracted X-rays.

2.3.5 Point and bulk initiation

There are two ways of starting SHS reactions: point initiation, where the green mixture is ignited at one end using a match or a hot wire, or bulk initiation where the green mixture is heated in a furnace (see Chapter 1, Section 1.2.1). In the experiments performed for this thesis the reactions were normally initiated at a point with a match. In some situations it was more practical to use a hot wire; a length of nichrome wire was connected via two copper rods to a d.c. power supply and typically 15 V, 1.5 A was required. The bulk initiation method tended to be used when point initiation failed. A Carbolite rapid heating furnace was used to bulk initiate the reactions. The green mixture was placed in a ceramic boat inside the furnace and the temperature was increased up to (say) 1200 °C. It was kept at that temperature for a few seconds before being allowed to cool to room temperature. Bulk initiated products did not require subsequent annealing.
2.4 *In-situ analysis of reactions*

2.4.1 *Temperature and velocity measurements*

The temperature and velocity of the SHS propagation wave were measured. The reaction temperature was measured by a Cambridge Instruments disappearing filament optical pyrometer and by a FLIR Systems Ltd. thermal imaging camera. Velocity measurements were made by recording video footage of the reactions and noting the time taken for a known length or a fixed mass of green mixture to react, to calculate the average velocity. Because the propagation wave travelled down into the bulk of the material, as well as along the length of the green mixture, the reaction velocity had to be carefully defined. The time taken for the reaction was defined as the time from ignition to when the final glow from within the reacting material disappeared. The pyrometer measurements were not very precise with errors estimated to be ± 100 °C, and errors for the thermal imaging camera estimated to be ± 10 °C. Both of these techniques measure surface temperature, so do not necessarily reflect the reaction temperature within the bulk of the powder or pellet. Indeed, it is difficult to measure such internal reaction temperatures and requires the use of, for example, specialist microthermocouples (which were not available for this study).

2.4.2 *Time-resolved X-ray diffraction (TRXRD)*

Time-resolved X-ray diffraction (TRXRD) experiments allowed rapid collection of XRD data of SHS reactions *in situ*. Experiments were performed at Daresbury Laboratory on Station 16.4 (July 1999, September 2000 and February 2001) and at the ESRF on Beamline ID-11 (November 2000). The experiment set-ups varied in detail, although both made use of the high intensity of synchrotron radiation and required fast readout of the collected data. Reactions were performed on powders and pressed pellets of green mixture, in zero field, 0.2 T and 1.1 T. The relationship between the incoming and diffracting X-rays and the SHS wave propagation is shown in Figure 2.6.
Figure 2.6 – Time-resolved X-ray diffraction experiments, plan view.

2.4.3 TRXRD – Daresbury Station 16.4

The Daresbury 16.4 experiments used a white beam of X-rays ($\lambda = 10^{-10}$ to $10^{-11}$ m, $E = 5$ to 112 keV), and three energy sensitive detectors (each with 4000 channels) fixed at low angles (of 2°, 5° and 8° 2θ). The experimental arrangement is shown in Figure 2.7. The Synchrotron Radiation Source (SRS) at Daresbury is an electron storage ring, which provides synchrotron radiation over a range of wavelengths of the electromagnetic spectrum. The electrons in the storage ring have an energy of 2.0 GeV with a current of 150-300 mA. The SRS was used in the multibunch mode of operation.

Figure 2.7 – TRXRD set-up at Daresbury Station 16.4.
The beam passed through the powder at 90° to the direction of propagation of the SHS wave, sampling either the starting material, the wave, or the region behind the wave. (This is certainly the case for the zero field reactions, but for the applied field reactions the direction of the wave relative to the beam is not clearly defined.) A metal plate with a pinhole was used to collimate the X-ray beam. The beam spot size was dependent on the size of the pinhole used (0.5, 1 or 2 mm). A typical exposure time for each diffraction pattern (scan) recorded in an SHS run was 0.25 s. The detector readout time for each scan varied from 1.9 s for the July 99 experiment, to 0.75 s in September 2000 and 0.24 s in February 2001. (The readout time was found by checking a time stamp file created when each scan in a run was recorded.) These improvements were due to only using one detector rather than three, and to changes made by the support staff at Daresbury in the way the data was read out. The maximum number of scans that could be recorded in a single run was 512, although typically 50-200 scans were used.

The green mixture was placed on a ceramic boat for zero field reactions, or inside a quartz tube in either the 0.2 T or 1.1 T applied magnetic field arrangements. The ceramic boat or magnet was mounted on an x-y-z-translation stage, which allowed the whole assembly to be moved relative to the beam. This allowed the sample to be positioned at the focal point, but it also meant that different positions within the green mixture sample could be scanned to check its homogeneity. The sample was placed 20 cm from the detectors, then its position was fine-tuned by small movements along the beam axis to maximise the flux to the detectors. A silicon standard was used to calibrate the detectors.

Reactions were performed on green mixtures in either powder or pellet form. Pellets were made by pressing 1 g amounts in 13 mm diameter dies to ~75 MPa pressure. The resulting pellets were about 2 mm thick. They were ignited by a nichrome wire, with a small amount of silicon grease and titanium placed on the end of the wire to aid ignition.
An important factor to take into account was the sample thickness. The diffracted X-ray signal collected by the detectors came from a lozenge shaped region of the sample, formed by the overlap of the incoming and outgoing X-ray beams. The lozenge length varied depending on the detector angle – the top detector sampled the shortest lozenge of sample. The lozenge length was also dependent on the beam spot diameter and was calculated to be between 5 and 24 mm for beam spot diameters of 0.5 mm and 2 mm respectively. Green mixture sample thicknesses of ~5 mm for powders, or ~2 mm for pellets, were used as a compromise between maximising the diffracted X-ray intensity and minimising the attenuation by the rest of the sample thickness.

The reactions had to be ignited remotely, so a hot electric wire was used; the current was turned on outside the experiment hutch. The reactions were monitored by cameras inside the hutch. To collect the data, a pre-SHS single scan would be taken, then the SHS reaction multi-scan of ~100 fast scans, followed by a post-SHS single scan.

2.4.4 TRXRD – ESRF Beamline ID-11

The ESRF ID-11 experiments used a monochromatic X-ray beam, \( \lambda = 0.2952 \, \text{Å} \) (\( E = 42 \, \text{keV} \)) monochromated by a silicon crystal, with a spot size of 0.2 x 0.2 mm\(^2\). The synchrotron at the ESRF is an electron storage ring; the electrons have an energy of 6.0 GeV and the beam current is 200 mA. The beam passed through the powder at 90° to the direction of propagation of the SHS wave sampling either the starting material, the wave, or the region behind the wave. (This is certainly the case for zero field reactions, but for applied field reactions the direction of the wave relative to the beam is not so clearly defined.) The diffracted rays were collected by a position-sensitive detector: a 1024 x 1024 channel CCD (charge-coupled device) camera, as shown in Figure 2.8.
The time resolution depended on the exposure time of each scan; a typical readout time was 80 ms (for a 50 ms exposure). A maximum of 250 scans could be collected in one series, so for a 50 ms exposure plus 80 ms readout, this corresponds to 32.5 s total time recorded. (The readout time was calculated by measuring the total time to record the 250 scans.) The sample was mounted in the same way as for the Daresbury experiments. The sample position relative to the detector did not have to be any particular value, although a fixed distance was used so that the angle range of the detector remained the same. A camera was used to watch the reactions. Also, the diffraction rings collected at the detector could be viewed “live” on a monitor. A silicon standard was used to calibrate the detector.

Reactions were performed on powders and pressed pellets of green mixture. Pellets were made by pressing ~1 g amounts of green mixture in 13 mm diameter dies to ~75 MPa. They were ignited by using a green mixture powder as a “fuse” leading up to and touching the pellet, with the nichrome wire placed in the powder. A higher flow rate of oxygen was required to ignite the pellets, of about 8 l min⁻¹, compared to 2 or 4 l min⁻¹ for powders.

In a similar way to the experiments at Daresbury, to collect the data at the ESRF a pre-SHS single scan was taken, then the SHS reaction multi-scan of 250 fast scans, followed by a post-SHS single scan.
2.5 Characterisation of products

The post-SHS and annealed products could be characterised in many ways. Brief details of the characterisation methods used are given below.

2.5.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) experiments were performed on a Philips X-pert 0-2θ diffractometer, with an accelerating voltage and current of 40 kV and 30 mA. Cu-Kα X-rays were used, in the reflection mode, with \( \lambda \) (average) = 1.54186 Å. A monochromator (and sometimes a Ni filter as well) was used to remove the β lines. The irradiated length was fixed at 10 mm. The powder sample was placed in a steel sample holder, 16 x 16 mm\(^2\), 1 mm deep, and was levelled with a glass slide. The diffracted X-rays were detected with a xenon-filled proportional counter. X-ray diffraction patterns were identified using the PC-APD search-match software,\(^{73}\) and by manual comparison with the JCPDS-ICDD database\(^{74}\) using the program PCPDFWIN.\(^{75}\) Lattice parameters were calculated using the program Unit Cell.\(^{76}\)

2.5.2 X-ray diffraction at Daresbury Station 9.1

Some X-ray diffraction analysis was performed with an image plate camera system at Daresbury Laboratory, Station 9.1. High quality diffraction patterns could be collected within minutes due to the intensity of the synchrotron X-ray source. Samples were loaded into quartz capillary tubes and positioned in the X-ray beam. The wavelength was \( \lambda = 0.6920 \) Å, monochromated by a silicon crystal. Diffraction patterns were collected for 10-30 minutes, with the diffracted rays recorded on a curved image plate. The intensities around the rings were integrated to produce a 2D intensity vs. angle plot of each diffraction pattern.

2.5.3 Vibrating sample magnetometry (VSM)

Vibrating sample magnetometry (VSM) was performed on an Aerosonic 3001 magnetometer, calibrated with a nickel foil. Hysteresis loops were recorded using an applied field of 5 kOe and a ramp rate of 20 Oe s\(^{-1}\). Measurements were performed on samples pressed into pellets (~50 MPa) and attached to the PEEK rod sample holder with PTFE tape. (PEEK – the name refers to
polyetheretherketone — is a non-magnetic plastic.) The maximum magnetisation $\sigma_{\text{max}}$ (emu g$^{-1}$) at 5 kOe, remanent magnetisation $\sigma_{\text{rem}}$ (emu g$^{-1}$) and coercive field $H_c$ (Oe) were calculated from the results. Errors were estimated as ± 0.1 emu g$^{-1}$ for the magnetisation and ± 10 Oe for the coercive field.

2.5.4 Mössbauer spectroscopy

Transmission $^{57}$Fe Mössbauer spectroscopy was performed using a Wissel MR-260 constant acceleration spectrometer. A $^{57}$Co source was used to supply $\gamma$-rays, by decaying to $^{57}$Fe. The 14.4 keV $\gamma$-rays were selected by a Single Channel Analyser sweep. A small amount of powder sample was mixed with boron nitride powder and packed into a 2 cm diameter plastic holder. For barium ferrite the ideal amount of powder to use was 65 mg, calculated using the program Recoil. The spectra were calibrated relative to $\alpha$-Fe foil at room temperature. Spectra were recorded in 512 channels by a krypton-filled proportional counter and were folded to remove baseline curvature. The spectra were analysed with a least-squares fitting program using Lorentzian lineshapes. In the fitting, quadrupole interactions were treated as a first-order perturbation to the magnetic interactions.

2.5.5 Scanning electron microscopy (SEM) / Energy dispersive X-ray analysis (EDAX)

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) were performed on a Hitachi S-570 instrument. The samples — post-SHS powders or fused material — had to be demagnetised to avoid causing damage to the machine, which uses magnetic focussing. (Small magnetised particles flying into the focussing system would be harmful). Powder samples could be mounted on a sticky carbon surface on an aluminium stub. Alternatively, powder or fused samples could be mounted in resin, and polished. This gave the advantage of a smooth surface when taking measurements. The prepared samples were then coated with carbon to avoid charging up the surface by the electron beam. A cobalt standard was used to calibrate the detector for the EDAX measurements.
2.5.6 Electron microprobe analysis

Electron microprobe analysis was performed using a JEOL JXA-8600 Electron Microprobe Analyser. The instrument included EDAX capability, to allow analysis of spots of \( \sim 100 \times 100 \, \mu m^2 \) areas. A working voltage of 25 kV gave a spot about 4 \( \mu m \) wide and deep. Samples were demagnetised, set in resin, polished and carbon coated. Elemental composition maps were produced of areas of a few hundred \( \mu m^2 \).

2.5.7 Thermal analysis

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were performed at the Institute of Structural Macrokinetics and Materials Science, Chernogolovka, Russia on a SETARAM TAG24 combined DTA and TGA machine. A heating rate of 10 °C min\(^{-1}\) was used. The green mixture samples were placed in alumina pans and heated in an atmosphere of air.

2.6 Summary

In this chapter the reactions that were performed and the way they were analysed, both \textit{in situ} and after the reaction, have been described. This forms the basis of the experimental work described in the following three chapters. In Chapter 3, the influence of processing parameters such as the particle size and source of oxygen will be covered. The influence of the magnetic field on the reaction and the products will be discussed in Chapter 4. The \textit{in situ} time-resolved X-ray diffraction studies are described in Chapter 5.
3 The influence of processing parameters on SHS

3.1 Introduction

The aim of the work described in this chapter is to understand the influence of various processing parameters on the SHS reaction and products. In the literature, the motivation for understanding the influence of processing parameters is to control the reaction rate, aspects of the product formation such as the phase formed and its microstructure, porosity and particle size, and to understand ignition and propagation. The motivation here was that understanding the influence of the processing parameters would help us to understand and control what was happening in the reactions and ensure that the best procedure, for example efficient annealing and minimisation of impurity levels, was used.

The term “processing parameters” covers three main areas: the green mixture, the way the SHS reaction is performed, and the processing of the product. Green mixture parameters include reactant particle sizes and shapes; contact between the particles; porosity – related to green mixture density and compaction; stoichiometry; and use of dilutents. SHS reaction parameters include preheating of the green mixture; method of initiation (point or bulk); the medium on which the reaction is performed and its surroundings; and the direction of the propagation wave. Product processing parameters include annealing and densification. Each of these types of processing parameter is discussed below.

3.1.1 Green mixture parameters

The influence of the size of the reactant particles has been considered by a number of authors. Figure 3.1 shows the reaction rate vs. metal particle diameter for a variety of reactions. As the reactant particle size decreases, the propagation rate (velocity) and combustion temperature increase. Smaller particles lead to higher reaction rates due to their higher surface area to volume ratio. They have a smaller maximum diffusion barrier. Also, for those reactions which proceed via melting, smaller particles undergo more complete melting than larger particles, leading to an increased reaction rate. In some cases, reducing the particle size
beyond a certain point does not lead to further increase of the reaction rate. An example is the reaction to form TiB$_2$ where the reaction rate stops increasing for particles $< 50$ $\mu$m in diameter, see Figure 3.1.

![Figure 3.1 - Reaction rate vs. metal particle diameter for a variety of SHS reactions (from Rice)].

The particular phase formed can depend on the particle size. For example, in the Ti-Si SHS system, use of Ti particles smaller than 100 $\mu$m led to Ti$_5$Si$_3$ as the product, whereas using larger Ti particles led to TiSi$_2$ + Ti.$^{12,79}$ (The reasons for this are not fully understood). The mode of combustion was also affected, changing from a stable to a spinning mode of propagation (see Chapter 1, Section 1.2.1) as the Ti particle size increased.$^{80}$ Increasing particle size has also been
observed to increase the wavefront width.\textsuperscript{11} The shape of the reactant particles is another important factor. Rice\textsuperscript{81} showed that foil sheets or flakes of Ti or C prevented ignition.

Relative particle sizes affect the contact between the particles. Particle contact is important because it determines the thermal conductivity of the green mixture, phase formation and product microstructure. An example is the reaction of TiO\textsubscript{2}, Al and C to form TiC and Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{11,82} It is thought to be initiated by the reaction between TiO\textsubscript{2} and Al. The situation is shown in Figure 3.2 for two different sizes of carbon particles. When small carbon particles were used they acted as a continuous phase and coated the larger Al particles, thereby preventing the TiO\textsubscript{2} particles from reacting with the Al. When the carbon particle size was increased, so that the TiO\textsubscript{2} became the continuous phase, the reaction rate increased. This was due to better contact between the TiO\textsubscript{2} and Al, and higher thermal conductivity of the mixture (due to TiO\textsubscript{2} having a higher thermal conductivity than C).

![Diagram of particle sizes and contact](image-url)

Figure 3.2 – Relationship between relative particle sizes and contact between different particles (from Bowen and Derby\textsuperscript{82}): (a) small carbon particles (carbon black), (b) larger carbon particles (graphite).
The compaction or densification of the green mixture affects the contact between the particles. The effect of densification depends on the system. It can improve reaction rates due to better inter-particle contact, hence better thermal conductivity, but can also reduce reaction rates if the thermal conductivity becomes too high, or if a gaseous reactant is unable to enter the green mixture.

Figure 3.3 shows the reaction rate vs. density of the reactant compact for a variety of SHS reactions. Most reactions exhibit a maximum in the reaction rate as a function of density.

Figure 3.3 – Reaction rate vs. theoretical density of reactant compact (from Rice^\textsuperscript{13}). (The numbers in brackets refer to the particle sizes, in μm, of the cations and anions).
The stoichiometry of the reaction influences reaction rates and temperatures.\textsuperscript{4} It can affect the combustion mode as well, for example, in Ni-Al reactions a 1:1 Ni:Al ratio gives steady state combustion whereas 3:1 or 1:3 gives a pulsating mode, or no reaction at all.\textsuperscript{4}

Dilutents are sometimes used in SHS reactions. The diluent may be one of the products from the reaction, an excess of a reactant, or an inert filler.\textsuperscript{78} Dilutents are used to control the velocity of SHS reactions. They work by increasing the thermal mass of the system and thereby reduce the adiabatic combustion temperature; they may also act as a barrier to inter-particle contact. Dilutents do not take part in the reactions themselves.\textsuperscript{11} An example is in the reaction of TiO\textsubscript{2}, Al and C to form TiC and Al\textsubscript{2}O\textsubscript{3}. Adding a 15 wt. % excess of Al\textsubscript{2}O\textsubscript{3} to the starting materials led to a decrease in the combustion velocity from 3.2 to 1.5 mm s\textsuperscript{-1} and a decrease in the combustion temperature from ~2100 °C to 2000 °C.\textsuperscript{5}

3.1.2 SHS reaction parameters

Two modes of SHS ignition are possible: point or bulk initiation. Reactions on point initiated systems show that the point chosen for ignition (e.g. the edge or centre of the green mixture), and hence the wave shape, can affect the product microstructure. For example, work by Bowen and Derby\textsuperscript{82} showed that planar wave propagation produced a planar laminar microstructure, whereas a spherical wave produced a spherical microstructure. The mode of combustion wave propagation (see Chapter 1, Section 1.2.1) can also influence the product structure; for example, the oscillating mode leads to a layered structure in the final product.\textsuperscript{4} In bulk initiated reactions the heating rate can influence the microstructure of the products.\textsuperscript{83}

Preheating is another way of controlling the reaction. It is used with weakly exothermic reactions to aid ignition, because it increases the combustion temperature, and hence the reaction rate and wave velocity.\textsuperscript{4,11} It has also been shown that the preheating temperature affects the microstructure\textsuperscript{84} and density\textsuperscript{82} of the product.
The medium on which SHS is performed may also influence the reaction and products. Rice$^{78}$ discusses some experiments where the supporting medium was changed from porous Al₂O₃ to dense Al₂O₃ and then a graphite brick, and this was found to reduce the propagation velocity of Ti + C reactions. The thermal conductivity of the surroundings therefore affects the reaction rate.

Sample size is also a factor that influences SHS reactions. For experiments performed on compacted pellets of green mixture, increasing the pellet diameter led to increased propagation wave velocities. An example is for reactions to form NiAl, where increasing the pellet diameter from 0.5 cm to 2 cm resulted in a 25 % increase in wavefront velocity.$^{78}$

The properties of the product in some cases have been seen to depend on the direction of the SHS wave, i.e. the wave can induce anisotropy in the product. For example, oxide samples cut parallel and perpendicular to the SHS propagation wave direction had different dielectric permeability and electroresistivity values.$^{85}$

3.1.3 SHS product parameters

SHS products are typically porous which means there are spaces (voids) between the particles. Porosity in the product can arise for a number of reasons: from porosity in the reactant materials, from outgassing of impurities, or from a reduction in density (if the theoretical density of the products is higher than that of the reactants). Porosity can be a useful feature, for example in catalysts, but often dense products are required. Sintering densifies the porous powder. In sintering the powder is heated and the particles fuse together to form larger particles. In a two step densification process, sintering of the powder product follows SHS. Various methods exist for the single step simultaneous SHS reaction and densification to form dense bodies. Examples are shock compression, hot rolling, isostatic pressing and hot pressing.$^{11}$ Many of these methods involve the production of a liquid phase.
3.1.4 Ways to observe the influence of processing parameters

Ways of observing the influence of processing parameters fall into two categories: studies of the reactions in situ, and studies of the products formed. In situ it is possible to study structure and phase formation, temperature profiles (as a function of position and/or time), average and instantaneous velocities and ionisation processes. Examples of how these techniques have been used in the literature are discussed below. Studies of the products formed include standard materials characterisation techniques (XRD, SEM, etc); the structure, morphology, porosity and microstructure of the product are of particular interest. These techniques are well known and will not be discussed further.

In situ studies of structure and phase formation have been performed by time-resolved X-ray diffraction (TRXRD). Sometimes TRXRD is combined with infra red thermography, to obtain simultaneous measurements of the temperature which can be correlated with the X-ray diffraction data. An infra red camera recorded images (5 or 30 frames s\(^{-1}\)) with a spatial resolution of 1 x 1 mm\(^2\) or better, to give a temperature profile relative to space or time. Another way of measuring temperature is to use microthermocouples. Either W/Re\(^{58}\) or Chromel/Alumel\(^{57}\) thermocouples have been used in the literature, with 100 \(\mu\)m diameter wire. These were embedded into the sample compact to ensure more accurate measurements, and were placed away from the hot ignition source. The maximum combustion temperature can thus be measured.

If two microthermocouples are used, the wave front velocity can be obtained. Another way to measure the average wave front velocity is to record the reaction with a video camera. An advanced video recording technique is digital high speed microscopic video recording. In this work, a high speed video camera (50-12000 frames s\(^{-1}\)) attached to a microscope, was used to record reactions. It provided a spatial map of the instantaneous wave front velocity, and allowed the authors to identify different types of wave propagation behaviour that were undetected on a macroscopic scale.
Ionisation processes during SHS have been measured by electrodes placed in the sample. The measured potential difference vs. time profile is dependent on the number, charge, density and distribution of the ions.

One other technique that is worth noting is quenching. This is a quasi-	extit{in situ} method, as it involves stopping the reaction by a rapid cooling of the reaction front. The reaction mechanism can be elucidated from SEM analysis of the sample at various points along the direction of wave propagation.

### 3.2 Experimental

Experiments were performed to investigate the influence of particle sizes, BaO$_2$ excess, oxygen source, oxygen flow rate and annealing conditions on the SHS reaction of BaO$_2$, Fe and Fe$_2$O$_3$, and the products. Experiments were also performed to compare BaFe$_{12}$O$_{19}$ made by SHS with BaFe$_{12}$O$_{19}$ made by conventional ceramic synthesis.

#### 3.2.1 Reactant particle sizes

The particle size of the reactants is known to be an important parameter in solid state reactions, determining the reaction rate and the phase formation. Experiments were performed to identify the influence of the Fe particle size on the reaction of BaO$_2$, Fe and Fe$_2$O$_3$, and the product. The following Fe sizes were used: $< 10 \, \mu$m, $44 \, \mu$m (325 mesh) and $500-2000 \, \mu$m (10-30 mesh). Also, some of the $< 10 \, \mu$m Fe powder was ball milled in an attempt to reduce its particle size; those reactions were also performed with ball milled Fe$_2$O$_3$. Ball milling was done in syalon ball mills. (Syalon is a proprietary ceramic material with the formula Si$_{6-x}$Al$_x$O$_3$N$_{8-x}$.) These were containers with lids and six small (~1 cm diameter) balls inside. The iron and iron oxide were put into two separate ball mills and sealed under argon, to avoid oxidation during the milling stage. The powders were milled for 30 hours. Barium ferrite green mixtures were made using the different particle sizes of iron, and SHS reactions were performed in zero field (ZF) and in a 1.1 T applied magnetic field (AF). The ease with which each green mixture reacted was noted. Reactions were also performed by bulk initiation in a furnace, due to difficulties in point initiation for some of the green mixtures.
3.2.2 \textit{BaO}2 \textit{excess}

In the SHS reactions to form \textit{BaFe}_{12}\textit{O}_{19} it has been found necessary to use an excess of \textit{BaO}. In the reactions performed for this thesis a 10 \% \textit{BaO} excess was used, which corresponds to a \textit{Ba:Fe} ratio of 1:10.9. In previous work by the UCL group\textsuperscript{66} a 1:9 \textit{Ba:Fe} ratio had been used, which corresponds to a 30 \% \textit{BaO} excess. In those reactions equal molar ratios of \textit{Fe} and \textit{Fe}_2\textit{O}_3 were used, whereas here a 2:1 ratio of \textit{Fe}:\textit{Fe}_2\textit{O}_3 was used. With a 10 \% excess of \textit{BaO} in the green mixture, \textit{BaFe}_2\textit{O}_4 was consistently observed as an impurity in the annealed product, at \textasciitilde2 \%. Perhaps this impurity could be removed by using a smaller excess of \textit{BaO}; this was the idea behind this set of experiments. Barium ferrite green mixtures were made containing 10 \%, 5 \% or zero \textit{BaO} excess. The molar amounts are given in Table 3.1. It should be noted that the \textit{BaO} powder is quoted as being 95 \% pure, which modifies the excess amounts (e.g. 10 \% excess is a 5 \% "true excess").

Table 3.1 – Amounts of the reagents used in green mixtures with different amounts of \textit{BaO}2 \textit{excess}.

<table>
<thead>
<tr>
<th>Excess of \textit{BaO}</th>
<th>Molar amounts / mmol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>\textit{BaO}</td>
</tr>
<tr>
<td>Zero</td>
<td>7.4</td>
</tr>
<tr>
<td>5 %</td>
<td>7.8</td>
</tr>
<tr>
<td>10 %</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Reactions were performed in zero field and 1.1 T applied magnetic field. The products were annealed at 1150 °C for 6 hours. X-ray diffraction measurements were performed on the annealed samples to identify any (crystalline) impurity phases present. DTA and TGA measurements were also taken of a barium ferrite reaction with 10 \% \textit{BaO} excess, as well as a reaction of \textit{Fe} + \textit{Fe}_2\textit{O}_3 in a 2:1 ratio (i.e. like the barium ferrite reaction but without any \textit{BaO}).

3.2.3 \textit{Oxygen source}

Since the ferrites are oxides, a vital factor is the accessibility of oxygen during their formation. Oxygen is the reagent that determines how far the reaction goes to
completion, hence the oxygen source is important. In SHS, the oxygen may come from the air, an oxygen gas supply or an internal oxidising agent. SHS reactions were performed with oxygen from these three different sources to investigate how the oxygen source influences the reaction and the products.

Reactions were performed on \( \text{BaFe}_{12}\text{O}_{19} \) green mixtures in zero field and 1.1 T applied magnetic field, in air, an oxygen gas flow, or with sodium perchlorate as an internal oxidising agent. Reaction temperatures were measured by optical pyrometry, and reaction velocities were found by measuring the length of green mixture and the time taken to react (from ignition to the disappearance of the glow from the reacting material). The length of material inside the magnet was measured by placing a piece of paper down each end of the quartz tube (like a dipstick) and subtracting those lengths to find out the length of the powder inside. The products were analysed by XRD, VSM, Mössbauer spectroscopy and electron microprobe analysis.

3.2.4 Oxygen flow rate

The oxygen flow rate experiments were designed to quantify how oxygen affects the reaction and the products. The source of oxygen had been shown to affect the reaction temperature and velocity. It was anticipated that the rate of oxygen flow into the system would be an important parameter. Previously the flow rate had not been measured.

Reactions were performed on equal masses of \( \text{BaFe}_{12}\text{O}_{19} \) green mixture (2.5 g) in zero field and 1.1 T applied magnetic field, under different flow rates of oxygen. The set-up is shown in Figure 3.4. A Platon oxygen flowmeter was used to set the \( \text{O}_2 \) flow rate to 0, 2, 6 or 10 l min\(^{-1}\). The distance between the gas nozzle and the reaction site was kept constant (13 cm). Reaction temperature was measured by optical pyrometry. The reaction velocity was measured in two ways: by measuring the time taken for known lengths, or fixed masses, of green mixtures to react, observed by video camera recording. The products in the applied field were found to contain two macroscopically distinct parts: a fused, shiny part and a brown coloured, matt part.
Figure 3.4 – Set-up for oxygen flow rate experiments in a 1.1 T magnetic field.

These parts were manually separated and weighed, to see if the amount of the shiny phase followed a trend with increasing flow rate. (Each reaction was performed twice, to get an idea of reproducibility.)

3.2.5 Annealing temperature and time

In the SHS formation of BaFe_{12}O_{19}, two steps are required – SHS followed by annealing. The annealing step is necessary because the reaction does not go to completion in the SHS step. Annealing conditions of 1150 °C and 6 hours had been used, although this choice of temperature and time had not been optimised. To find the lowest temperature and shortest time required to produce single phase BaFe_{12}O_{19}, post-SHS products were annealed at different temperatures and for different lengths of time.

Several reactions were performed in zero field on the BaFe_{12}O_{19} green mixture, to produce enough post-SHS product to use in these experiments. The post-SHS products were ground up and divided into equal masses (0.25 g), then placed in ceramic boats. These powders were put into the furnace at 800 °C for 2 hours, 1000 °C for 30 minutes or 2 hours, and 1200 °C for 5 minutes, 30 minutes or 2 hours. They were removed at high temperature, rather than being allowed to cool, to get a fair idea of how the time spent at high temperature influences the phases formed. The high temperatures being used necessitated various safety precautions: wearing of safety glasses, sunglasses (due to exposure to bright light
from the hot furnace) and a face shield; asbestos gloves and long tongs, to remove ceramic boats safely from the furnace while at high temperature; and placing a ceramic mat next to the furnace, to put the hot boats on.

3.2.6 Conventional ceramic synthesis

\[ \text{BaCO}_3 + 6 \text{Fe}_2\text{O}_3 \rightarrow \text{BaFe}_{12}\text{O}_{19} + \text{CO}_2 \]  
Eqn. 3.1

Barium ferrite was also made by the standard ceramic processing method, to compare the product with that obtained by self propagating high temperature synthesis (SHS). Powders of \( \text{BaCO}_3 \) (0.421 g, 2.1 mmol) and \( \text{Fe}_2\text{O}_3 \) (2 g, 12.5 mmol) were ground together with a pestle and mortar, according to Eqn. 3.1. The mixture was heated in a furnace at 1200 °C for 2 hours. The resultant black powder was then reground prior to analysis by XRD, VSM and Mössbauer spectroscopy.

3.3 Results

3.3.1 Reactant particle sizes

As the Fe particle size increased, SHS propagation became more difficult. In fact the reaction would not propagate with the largest size Fe powder (500-2000 μm). The green mixture containing ball milled Fe did not propagate easily in zero field. To enable the influence of Fe particle size to be studied, the green mixtures were bulk initiated in a furnace, due to the difficulties in point initiation for the larger particles that were used (some reactions failed to propagate). The samples were heated from room temperature to 1200 °C at a rate of 50 °C min\(^{-1}\) and kept there for 10 s. The furnace was then switched off and the products were left to cool overnight.

Mössbauer spectroscopy was performed on the furnace-reacted samples. Comparisons of the areas in the Mössbauer spectra give an idea of the relative amounts of the various phases in each product. It was found that as Fe particle size increased (not including the ball milled Fe) the amount of the \( \text{BaFe}_{12}\text{O}_{19} \)
phase decreased while the amount of the BaFe$_2$O$_4$ phase increased, see Table 3.2. It is notable that BaFe$_{12}$O$_{19}$ is produced in the SHS step by bulk initiation, but not by point initiation.

Table 3.2 – Phase composition of barium ferrite furnace-reacted (bulk initiated) products produced with different sizes of Fe particles. Furnace reaction includes partial annealing.

<table>
<thead>
<tr>
<th>Bulk initiated barium ferrite sample made with:</th>
<th>Phases present in product as identified by Mössbauer analysis, relative areas % (± 0.5 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball milled Fe and Fe$_2$O$_3$</td>
<td>BaFe$<em>{12}$O$</em>{19}$ 67.9  Fe$_2$O$_3$ 23.6  BaFe$_2$O$_4$ 4.0  Doublet* 4.5</td>
</tr>
<tr>
<td>&lt; 10 µm Fe</td>
<td>BaFe$<em>{12}$O$</em>{19}$ 89.9  Fe$_2$O$_3$ 8.7  BaFe$_2$O$_4$ 1.4  -</td>
</tr>
<tr>
<td>44 µm Fe</td>
<td>BaFe$<em>{12}$O$</em>{19}$ 66.6  Fe$_2$O$_3$ 24.5  BaFe$_2$O$_4$ 8.8  -</td>
</tr>
<tr>
<td>500-2000 µm Fe</td>
<td>BaFe$<em>{12}$O$</em>{19}$ 57.1  Fe$_2$O$_3$ 7.0  BaFe$_2$O$_4$ 28.5  Doublet* 7.3</td>
</tr>
</tbody>
</table>

*Doublet: the measured quadrupole splittings were ca. 0.6 mm s$^{-1}$, which is typical of ferric iron oxide in the paramagnetic or superparamagnetic state. Given that the measurements were at room temperature, it is more likely that the doublets are due to fine particle material in the superparamagnetic state.

VSM measurements on the furnace-reacted products show that with the largest Fe particle size (500-2000 µm) there is a significant increase in the maximum magnetisation, from 36 emu g$^{-1}$ to 86 emu g$^{-1}$, and a reduction in the coercivity, 2.9 kOe to 1.7 kOe, compared to the usual Fe particle size (< 10 µm).

3.3.2 BaO$_2$ excess

The annealed samples prepared with 5 % BaO$_2$ excess showed BaFe$_2$O$_4$ and Fe$_2$O$_3$ impurities, whereas the zero excess samples showed mostly Fe$_2$O$_3$ impurity, with a little BaFe$_2$O$_4$. Estimates of the amounts of each impurity found by Mössbauer and XRD analysis are given in Table 3.3. The XRD patterns are shown in Figure 3.5.
Table 3.3 – Amounts of impurity phases in annealed products as a function of BaO\(_2\) excess in BaFe\(_{12}\)O\(_{19}\) green mixture, identified by XRD and Mössbauer analysis.

<table>
<thead>
<tr>
<th>BaO(_2) excess in green mixture %</th>
<th>XRD approx. peak intensity %</th>
<th>Mössbauer area %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BaFe(_2)O(_4)^a Fe(_2)O(_3)^b Fe(_2)O(_3)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>5 5 10</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>5 5 8</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>2 0 0</td>
<td>0</td>
</tr>
</tbody>
</table>

*a* – see peaks at \(\sim-28^\circ\) in Figure 3.5  
*b* – see peaks at \(\sim-33^\circ\) in Figure 3.5

Figure 3.5 – XRD patterns of annealed barium ferrite applied field (shiny) products, made with (a) zero % and (b) 5 % excess of BaO\(_2\).

The DTA and TGA results for the reactions of BaO\(_2\) + Fe + Fe\(_2\)O\(_3\) and Fe + Fe\(_2\)O\(_3\) in air are shown in Figure 3.6. The TGA data shows a mass increase of about 12 % in both reactions, which begins at \(\sim300^\circ\)C and continues up to \(\sim750-800^\circ\)C. In the reaction of Fe + Fe\(_2\)O\(_3\) the mass then remains constant, but in the reaction that also contains BaO\(_2\) some mass is lost from the system, finishing at \(\sim3\) % greater than the starting mass. The DTA data shows an exothermic peak for both reactions at 400-440 °C, which corresponds to the temperature of maximum oxidation.
3.3.3 Oxygen source

The temperature and velocity measurements for reactions performed with different oxygen sources are given in Table 3.4. The reaction temperature and velocity increased as the oxygen source changed from air to oxygen to perchlorate.
Table 3.4 – Influence of different oxygen sources on the temperature, colour and velocity of the SHS wave for reactions on barium ferrite green mixture in zero field (ZF) and 1.1 T applied field (AF).

<table>
<thead>
<tr>
<th>Oxygen source</th>
<th>Temperature(^a)/°C</th>
<th>Colour</th>
<th>Velocity(^b)/mm s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium ferrite, ZF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>850</td>
<td>Orange</td>
<td>0.4</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>975 / 920(^d)</td>
<td>Orange</td>
<td>1.0</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>1100-1150</td>
<td>Yellow</td>
<td>1.1-1.4</td>
</tr>
<tr>
<td>Barium ferrite, 1.1 T AF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>800</td>
<td>Dull orange</td>
<td>0.2</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>1200 / 1240(^d)</td>
<td>Yellow</td>
<td>0.2-0.25</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>1250</td>
<td>Orange</td>
<td>0.4-0.7</td>
</tr>
</tbody>
</table>

\(^a\) Temperature measured by optical pyrometry unless otherwise stated.

\(^b\) Velocity calculated by measuring the length of green mixture and dividing by the time taken for the reaction, from ignition to disappearance of glowing material from the bulk of the mixture.

\(^c\) \(\text{O}_2\) flow rate was not measured.

\(^d\) Thermal imaging camera measurements.

The products formed in air or under an oxygen flow in zero field were brown coloured and partly fused, but when perchlorate was used as the oxygen source the product was black and highly fused. For reactions in an applied field the air and oxygen reacted products were fibrous and contained shiny and matt regions. The perchlorate reaction products looked different, black and fused with only a small amount of shiny part, ~5-10% of the total amount of product. Photographs of the products are shown in Figure 3.7.
Figure 3.7 – Photographs of barium ferrite SHS products from: (a) zero field powder reaction, (b) 1.1 T powder reaction, side view, (c) 1.1 T powder reaction, end view of hourglass shape, (d) zero field powder reaction with sodium perchlorate as internal oxygen source, (e) 1.1 T reaction with sodium perchlorate, (f) zero field bar reaction with sodium perchlorate (1.1 T bar looked identical).

The microstructures of the different products varied. With the oxygen reactions there was an acicular, needle-like microstructure for the applied field post-SHS products, but for the perchlorate post-SHS products this microstructure was seen in zero field as well as applied field. See Figure 3.8.
The reactions were more complete when using perchlorate. No unreacted starting materials were observed in the post-SHS perchlorate products, whereas in the post-SHS oxygen products, about 40-50 % of the material was unreacted. This is shown in the Mössbauer patterns of the products synthesised with oxygen and with perchlorate, Figure 3.9. The greater degree of conversion in the perchlorate product can be seen – for example, it contains more BaFe$_2$O$_4$ and less Fe$_2$O$_3$ than the product made in an oxygen flow.
Figure 3.9 – Mössbauer patterns of barium ferrite applied field post-SHS samples, made with sodium perchlorate as an internal oxygen source (top) and with an oxygen gas flow (bottom) (shiny part). (Fe$_3$O$_4$-1 is the sextet due to Fe in the tetrahedral sites of Fe$_3$O$_4$ and Fe$_3$O$_4$-2 is due to Fe in the octahedral sites.)

The annealed products had different magnetic properties depending on the oxygen source. The coercive fields of the perchlorate products were reduced compared to the oxygen products, as shown in Table 3.5.

Table 3.5 – Influence of oxygen source on the magnetic parameters of the annealed BaFe$_{12}$O$_{19}$ products.

<table>
<thead>
<tr>
<th>Oxygen source for ZF SHS reaction</th>
<th>$\sigma_{\text{max}} / \text{emu g}^{-1}$ (± 0.1)</th>
<th>$\sigma_{\text{rem}} / \text{emu g}^{-1}$ (± 0.1)</th>
<th>$H_c / \text{Oe}$ (± 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen, 2 l min$^{-1}$</td>
<td>43.1</td>
<td>29.6</td>
<td>2240</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>46.5</td>
<td>30.4</td>
<td>1320</td>
</tr>
</tbody>
</table>
3.3.4 Oxygen flow rate

Measurements of the reaction temperature and velocity using different flow rates of oxygen are shown in Table 3.6, along with the amount of the product that was shiny. In this table the reaction velocities are expressed in two different ways. Velocities are expressed in mm s$^{-1}$ calculated from measurements of the length of green mixture and the time taken to react. The velocities are also expressed as the time taken for 2.5 g of green mixture to react. In both cases the time taken to react includes the time taken for the wave to travel along the surface of the green mixture as well as the slower reaction into the bulk of the material.

With increasing oxygen flow rate, the reaction temperature increased (more noticeably for applied field than zero field), the velocity increased, and the proportion of shiny part in the applied field post-SHS product increased. The VSM results for the annealed samples are given in Table 3.7. They show a reduced coercive field for the AF shiny parts compared to the ZF and AF matt parts, for all flow rates.
Table 3.6 – Effect of oxygen flow rate on the reaction temperature, velocity, time taken to react, and mass of shiny part in the product, for zero field (ZF) and 1.1 T applied field (AF) barium ferrite reactions.

<table>
<thead>
<tr>
<th>O₂ flow rate / 1 min⁻¹</th>
<th>Property measured</th>
<th>ZF</th>
<th>AF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature / °C</td>
<td>850</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Velocityᵃ / mm s⁻¹</td>
<td>0.42</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Time taken to reactᵇ / s</td>
<td>173</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Mass % of shiny part</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>Temperature / °C</td>
<td>975</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Velocityᵃ / mm s⁻¹</td>
<td>1.0</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Time taken to reactᵇ / s</td>
<td>58</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Mass % of shiny part</td>
<td>-</td>
<td>72, 54</td>
</tr>
<tr>
<td>2</td>
<td>Temperature / °C</td>
<td>1000</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td>Velocityᵃ / mm s⁻¹</td>
<td>1.54</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>Time taken to reactᵇ / s</td>
<td>39</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Mass % of shiny part</td>
<td>-</td>
<td>78, 72</td>
</tr>
<tr>
<td>6</td>
<td>Temperature / °C</td>
<td>1000</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>Velocityᵃ / mm s⁻¹</td>
<td>1.54</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Time taken to reactᵇ / s</td>
<td>37</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Mass % of shiny part</td>
<td>-</td>
<td>83, 78</td>
</tr>
</tbody>
</table>

ᵃ – Velocity calculated by measuring the length of green mixture and dividing by the time taken for the reaction, from ignition to disappearance of glowing material from the bulk of the mixture.

ᵇ – Time taken for 2.5 g of green mixture to react, from ignition to disappearance of glowing material, measured by analysis of video camera footage.
Table 3.7 – Effect of oxygen flow rate on the magnetic parameters of the annealed BaFe$_{12}$O$_{19}$ products.

<table>
<thead>
<tr>
<th>O$_2$ flow rate /1 min$^{-1}$</th>
<th>Product description</th>
<th>$\sigma_{\text{max}}$ / emu g$^{-1}$ (± 0.1)</th>
<th>$\sigma_{\text{rem}}$ / emu g$^{-1}$ (± 0.1)</th>
<th>$H_c$ / Oe (± 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>ZF</td>
<td>43.7</td>
<td>30.3</td>
<td>2430</td>
</tr>
<tr>
<td></td>
<td>AF</td>
<td>41.4</td>
<td>28.9</td>
<td>2370</td>
</tr>
<tr>
<td>2</td>
<td>ZF</td>
<td>43.1</td>
<td>29.6</td>
<td>2240</td>
</tr>
<tr>
<td></td>
<td>AF matt</td>
<td>43.8</td>
<td>29.8</td>
<td>1980</td>
</tr>
<tr>
<td></td>
<td>AF shiny</td>
<td>43.3</td>
<td>28.7</td>
<td>1590</td>
</tr>
<tr>
<td>6</td>
<td>ZF</td>
<td>44.0</td>
<td>30.0</td>
<td>2190</td>
</tr>
<tr>
<td></td>
<td>AF matt</td>
<td>44.2</td>
<td>29.7</td>
<td>2070</td>
</tr>
<tr>
<td></td>
<td>AF shiny</td>
<td>42.4</td>
<td>27.2</td>
<td>1460</td>
</tr>
<tr>
<td>10</td>
<td>ZF</td>
<td>41.7</td>
<td>30.2</td>
<td>2160</td>
</tr>
<tr>
<td></td>
<td>AF matt</td>
<td>43.6</td>
<td>29.1</td>
<td>1760</td>
</tr>
<tr>
<td></td>
<td>AF shiny</td>
<td>43.9</td>
<td>28.5</td>
<td>1560</td>
</tr>
</tbody>
</table>
3.3.5 *Annealing temperature and time*

The products from annealing at different temperatures and times were analysed by XRD from 30-35° 2θ (this range was chosen to detect the presence of BaFe₁₂O₁₉). The phases observed are given in Table 3.8, and the XRD patterns are shown in Figure 3.10.

**Table 3.8 – Phases observed for different annealing temperatures and times of barium ferrite post-SHS products.**

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>5 minutes</th>
<th>30 minutes</th>
<th>2 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
<td>-</td>
<td>-</td>
<td>Mainly Fe₂O₃, maybe some BaFe₁₂O₁₉ at 10 % level</td>
</tr>
<tr>
<td>1000 °C</td>
<td>-</td>
<td>BaFe₁₂O₁₉ and Fe₂O₃ at similar levels</td>
<td>BaFe₁₂O₁₉ is main phase, Fe₂O₃ at 50 % level</td>
</tr>
<tr>
<td>1200 °C</td>
<td>BaFe₁₂O₁₉ is main phase, Fe₂O₃ at 20 % level</td>
<td>BaFe₁₂O₁₉ is main phase, Fe₂O₃ at 10 % level</td>
<td>BaFe₁₂O₁₉ is main phase, Fe₂O₃ at 5 % level</td>
</tr>
</tbody>
</table>

- denotes experiments that were not performed.
Figure 3.10 – XRD patterns for barium ferrite post-SHS product annealed at different temperatures and for different times: (a) 2 hours at 800 °C, (b) 30 minutes at 1000 °C, (c) 2 hours at 1000 °C, (d) 5 minutes at 1200 °C, (e) 30 minutes at 1200 °C, (f) 2 hours at 1200 °C.
3.3.6 *Conventional ceramic synthesis*

The barium ferrite product made by the ceramic route was analysed by XRD, VSM and Mössbauer spectroscopy. X-ray diffraction showed that nearly single phase \( \text{BaFe}_{12}\text{O}_{19} \) had been formed, with lattice parameters \( a = 5.8996(8) \) Å and \( c = 23.2304(58) \) Å. The Mössbauer spectrum was fitted with four sextets, corresponding to the five different sites for \( \text{Fe}^{3+} \) ions in \( \text{BaFe}_{12}\text{O}_{19} \), described in Chapter 1, Section 1.3.2. (The components due to the \( 4f_4 \) and \( 2a \) sites were not resolvable.) The \( 12k, 4f_4+2a, 4f_6 \) and \( 2b \) sites were fitted with relative areas in the ratio 12:6:4:1.5 respectively. An area of 1.5 rather than 2 was used for the \( 2b \) sites because they have a recoil free fraction that is lower than that for the other sites.92 The parameters are similar to those for an annealed \( \text{BaFe}_{12}\text{O}_{19} \) sample made by SHS, as shown in Table 3.9. The maximum magnetisation, remanent magnetisation and coercive field of the barium ferrite products made by SHS and ceramic synthesis are given in Table 3.10.
Table 3.9 – Comparison of Mössbauer parameters for BaFe$_{12}$O$_{19}$ products made by SHS and by conventional ceramic synthesis. The SHS product was annealed at 1150 °C for 6 hours; the ceramic synthesis product was heated to 1200 °C for 2 hours. Isomer shift $\delta \pm 0.01$ mm s$^{-1}$, quadrupole shift $2\varepsilon \pm 0.02$ mm s$^{-1}$, linewidth $\Gamma \pm 0.01$ mm s$^{-1}$, hyperfine field $B_{hf} \pm 1$ kG.

<table>
<thead>
<tr>
<th>Fe site</th>
<th>ZF SHS</th>
<th>Ceramic synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>12k</td>
<td>$\delta$</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>413</td>
</tr>
<tr>
<td>4f$_4$+2a</td>
<td>$\delta$</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>492</td>
</tr>
<tr>
<td>4f$_6$</td>
<td>$\delta$</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>514</td>
</tr>
<tr>
<td>2b</td>
<td>$\delta$</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 3.10 – Comparison of magnetic parameters for BaFe$_{12}$O$_{19}$ products made by SHS and by conventional ceramic synthesis. The SHS product was annealed at 1150 °C for 6 hours; the ceramic synthesis product was heated to 1200 °C for 2 hours.

<table>
<thead>
<tr>
<th></th>
<th>ZF SHS</th>
<th>Ceramic synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{max}}$ / emu g$^{-1}$ (± 0.1)</td>
<td>43.1</td>
<td>42.6</td>
</tr>
<tr>
<td>$\sigma_{\text{rem}}$ / emu g$^{-1}$ (± 0.1)</td>
<td>29.6</td>
<td>28.6</td>
</tr>
<tr>
<td>$H_c$ / Oe (± 10)</td>
<td>2240</td>
<td>3010</td>
</tr>
</tbody>
</table>
3.4 Analysis and Discussion

3.4.1 Reactant particle sizes

The idea behind ball milling the Fe and Fe$_2$O$_3$ was to produce smaller particles with more surface area, hence they would be expected to be more reactive. However, the mixture containing ball milled reagents was found to be less reactive than the mixture using <10 μm Fe. Possible explanations are that the iron oxidised during ball milling, or that the particles clumped together (agglomerated) during ball milling, reducing their effective surface area.

A trend was noted in the furnace-reacted products with reactant particle size. As the Fe size decreased, more BaFe$_{12}$O$_{19}$ was produced. Only the ball milled Fe was different and did not fit this trend. This could be due to agglomeration of the Fe and Fe$_2$O$_3$ particles during ball milling. In the case where the reaction went furthest to completion, the BaO$_2$ particles were the largest in the reaction, at 44 μm, followed by Fe particles at <10 μm and the Fe$_2$O$_3$ particles were the smallest at <5 μm. On the microscopic scale, the Fe$_2$O$_3$ particles probably coated the larger BaO$_2$ and Fe particles. Reactions at the interfaces would primarily be between Fe + Fe$_2$O$_3$ and BaO$_2$ + Fe$_2$O$_3$. However, if the Fe and Fe$_2$O$_3$ agglomerated during ball milling, this would lead to a reduction in the total surface area of the reactant particles, less interface contact and less coating of one particle with another type of particle. Therefore particle agglomeration is likely to lead to less favourable reaction conditions.

These experiments also showed that BaFe$_{12}$O$_{19}$ is made in the SHS step if the green mixture is bulk initiated in a furnace, but not if it is initiated at a point. This is because bulk initiation in a furnace effectively includes a period of annealing, because the mixture is at high temperatures for several minutes due to the slow cooling rate of the furnace.
3.4.2 \( \text{BaO}_2 \) excess

When a 10% excess of \( \text{BaO}_2 \) was used to synthesise \( \text{BaFe}_{12}\text{O}_{19} \), the annealed product consistently contained \( \text{BaFe}_2\text{O}_4 \) as an impurity, at \( \sim 2\% \). The aim of varying the amount of \( \text{BaO}_2 \) excess in the green mixture was to see if the impurity could be removed. However, when zero and 5% excesses of \( \text{BaO}_2 \) were used, the annealed products both contained \( \text{BaFe}_2\text{O}_4 \) and \( \text{Fe}_3\text{O}_4 \) impurities. It is possible to explain why annealing does not give 100% conversion to the desired \( \text{BaFe}_{12}\text{O}_{19} \) phase. One reason could be that the initial stoichiometry was incorrect – either there was too much or too little \( \text{BaO}_2 \) to begin with, particularly if the purity of the \( \text{BaO}_2 \) powder is taken into consideration. Another reason could be that the ratios of \( \text{BaFe}_2\text{O}_4 \) and \( \text{Fe}_3\text{O}_4 \) in the post-SHS product are correct, but that they are not sufficiently well mixed to form single phase \( \text{BaFe}_{12}\text{O}_{19} \). Some pockets of \( \text{BaFe}_2\text{O}_4 \) and \( \text{Fe}_3\text{O}_4 \) may remain even after annealing, since SHS is a solid state diffusion technique and the diffusion barrier has to be overcome.

The TGA results provided evidence that oxygen is lost during the barium ferrite reaction. \( \text{BaO}_2 \) is known to decompose at 800 °C,\(^9\) and this corresponds to the temperature at which the mass begins to decrease in the barium ferrite reaction, see Figure 3.6. Up to 800 °C the TGA results for the reactions of \( \text{Fe} + \text{Fe}_3\text{O}_4 \) and \( \text{BaO}_2 + \text{Fe} + \text{Fe}_3\text{O}_4 \) look similar, with a mass increase of 12%. This is equivalent to 1:1.27 moles of \( \text{Fe}:\text{O} \) in the product, and is consistent with \( \text{Fe}_3\text{O}_4 \) formation. Above 800 °C it is likely that \( \text{BaO} \) combines with \( \text{Fe}_3\text{O}_4 \) to form \( \text{BaFe}_2\text{O}_4 \). The mass decrease is due to oxygen loss when \( \text{BaO}_2 \) decomposes.

Differential thermal analysis (DTA) is used to measure the ignition temperatures for thermal explosion reactions (see Chapter 1, Section 1.2.2). However, for oxidation reactions such as those measured here, the concept of ignition is not clearly defined,\(^10\) and instead the temperature at which there is maximum oxidation is what is measured. For \( \text{Fe}/\text{Fe}_3\text{O}_4 \) and \( \text{BaFe}_{12}\text{O}_{19} \) reactions the maximum oxidation temperature was measured to be 400-440 °C.
3.4.3 Oxygen source

The reactions were observed to be hotter and faster as the oxygen source changed from air to oxygen to perchlorate, see Table 3.4. This is expected. With an oxygen gas supply there is an increased concentration of oxygen at the reaction site compared to air, which means that more oxygen is available to enter the system. With perchlorate, the source of oxygen is intimately mixed with the reactants. Instead of diffusing in from outside, as in the previous two cases, oxygen is released from within the powder when the sodium perchlorate decomposes (at 482 °C). The decomposition also generates heat, leading to increased reaction temperatures. Sodium chloride, NaCl, is produced and is a liquid at the SHS reaction temperatures (melts at 801 °C). It acts as a wetting agent and improves diffusion of the reactants. Melting of one or more of the reactants has been shown to increase the combustion rate in other SHS reactions, see for example Merzhanov or Varma et al.

Optical pyrometry and thermal imaging camera techniques measure the surface temperature. The internal temperature is hotter than the temperature measurements given in Table 3.4 suggest, but to accurately measure the internal temperature, very fine thermocouples and a large thermal mass would be required. Although they may not be strictly accurate, the temperature measurements given here provide valuable information about which reactions are hotter.

Besides reaction temperature, the oxygen source was also found to affect the appearance, microstructure and properties of the product. Comparisons are only drawn between the oxygen and perchlorate products, which comprised the most complete reaction sets. The shiny part that was observed in the post-SHS product when an external oxygen flow was used may be due to a glazing effect. Very little shiny part was seen when perchlorate was used, where the oxygen comes from the inside. The nature of the shiny part will be considered more fully in Chapter 4.

The phase composition, microstructure and magnetic properties of the products all point to the combustion being more complete when perchlorate is used compared
to oxygen. This fits in with the higher reaction temperatures observed for perchlorate reactions, which would lead to a greater degree of conversion of the reactants. The reduction in coercive field of the annealed product is attributed to better combustion leading to fewer pinning centres in both the post-SHS and annealed products. Pinning centres are generally defects in the crystalline structure, such as vacancies and interstitials (point defects), dislocations, non-magnetic inclusions or cavities, grain boundaries or dispersed phases. Fewer pinning centres means less resistance to domain wall motion, and consequently a lower coercive field.

3.4.4 Oxygen flow rate

With increasing oxygen flow rate, the reaction temperature increased (more noticeably for AF than ZF), the velocity increased, and the proportion of shiny part in the AF product increased.

The reactions in a 1.1 T applied magnetic field were faster than those in zero field at all flow rates of oxygen. Equal masses of green mixture reacted more quickly in AF than ZF, see Table 3.6. Comparing the time taken for equal masses of green mixture to react gives an indication of the relative rate of conversion of the reactants. The velocities quoted in mm s\(^{-1}\), from measurements of the length of green mixture and time taken for the reaction, give a less accurate picture of the true reaction velocities. This is because the SHS propagation wave travels both across the surface and down into the green mixture at different rates. In addition, the length and density of a given mass of green mixture is likely to be different in AF compared to ZF, which in turn would affect the velocity if expressed in mm s\(^{-1}\). Therefore, measurements of the time taken for equal masses of green mixture to react provide a more meaningful measure of the reaction velocity, than measurements in mm s\(^{-1}\).

X-ray diffraction patterns of the post-SHS AF products show that the shiny part is more fully combusted than the matt part. It has a greater degree of conversion, containing less of the starting materials and more of the combusted phases such as Fe\(_3\)O\(_4\) and BaFe\(_2\)O\(_4\). The proportion of shiny part was found to increase as the
oxygen flow rate increased, which means that the extent of reaction completeness in the SHS step increases with oxygen flow rate. The actual relative amounts of shiny and matt parts varied between the two repeat runs (i.e. 72-83 % for the first run and 54-78 % for the second run), although the percentage of shiny phase was seen to increase with oxygen flow rate for both runs.

The magnetic measurements of the annealed products show that the AF shiny parts have a reduced coercive field compared to the ZF and AF matt parts. The magnitude of this coercive field reduction was 27-33 %. However, no trend in the magnetic parameters was noticed with increasing flow rate.

3.4.5 Annealing temperature and time

Some of the post-SHS products described in this thesis were annealed at 1150 °C for 6 hours, before the temperature and time had been optimised. When annealing conditions of 1150 °C for 6 hours were used, the impurity that was normally seen was BaFe₂O₄. It may have been present in the samples tested here for the annealing temperature and time, but was not detected because its main peaks fall outside the 2θ range that was used. Whether 1200 °C for 2 hours or 1150 °C for 6 hours is chosen for annealing is unlikely to significantly affect the properties of the annealed products, although 1200 °C for 2 hours is the optimum temperature and time to produce virtually single phase BaFe₁₂O₁₉.

3.4.6 Conventional ceramic synthesis

The conventional ceramic synthesis technique, i.e. mixing BaCO₃ and Fe₂O₃ and heating them in a furnace to a high temperature, yielded a product which was similar in nature in most respects to that produced by SHS and subsequent annealing. The one significant difference between the products made by the two techniques was in their coercive fields, Hc. The coercive field of the ceramic synthesis product was found to be 3010 Oe, compared to 2240 Oe for the zero field annealed SHS product. SHS synthesis therefore gives products with reduced coercive fields compared to conventionally synthesised products. This might be due to impurities being expelled during the SHS process, leading to fewer pinning centres in the annealed product compared to the product formed in the furnace by
ceramic synthesis. The reduction of coercive field relative to the ceramic synthesis product is ~20-50 % for the products made by SHS in ZF and AF under different flow rates of oxygen (Table 3.7). The ability to modify the coercive field of a magnetic material is useful, particularly for applications such as magnetic recording.

3.5 Conclusions

The aim of this work was to investigate the influence of processing parameters on the SHS reaction of BaO$_2$, Fe and Fe$_2$O$_3$ in the presence of oxygen, and the products. Experiments were performed to study the effects of the reactant particle sizes and the amount of BaO$_2$ excess used in the green mixture, the source of oxygen and the flow rate of oxygen into the system during the reaction, and to find the optimum temperature and time to anneal the post-SHS product. SHS propagation was found to be easiest with <10 μm Fe particle size. Using larger particle sizes, propagation became more difficult and the bulk propagated products contained less of the barium ferrite phase. BaO$_2$ excesses of zero, 5 and 10 % all resulted in impurities in the annealed product. A 10 % excess was chosen for all other experiments. The choice of oxygen source affected the reaction temperature and velocity and the products formed. Reactions were found to be hotter and faster going from air to oxygen to perchlorate. The post-SHS products were found to be more fully combusted and the annealed products exhibited lower coercive fields, as the oxygen source changed in this way. Increasing the flow rate of oxygen also led to hotter and faster reactions and a more fully combusted product. However, the coercive field did not change as a function of flow rate. An annealing temperature of 1200 °C for a time of 2 hours was found to be the optimum to transform the post-SHS products into single phase BaFe$_{12}$O$_{19}$ (although annealing at 1150 °C for 6 hours also produces virtually single phase BaFe$_{12}$O$_{19}$). SHS was also compared with ceramic synthesis. Barium ferrite prepared by SHS was found to be similar to the product made by conventional ceramic synthesis, except that barium ferrite made by SHS had coercive field values about 20-50 % lower than the ceramic synthesis product.
4 The influence of magnetic fields on SHS

4.1 Introduction

At the start of this project, BaFe$_{12}$O$_{19}$ had been synthesised in a magnetic field of 1.1 T. The reaction in the field was observed to be hotter and faster than in zero field: ca. 1200 °C vs. 1000 °C and ca. 5 vs. 2 mm s$^{-1}$. The post-SHS applied field (AF) product from the reaction to form BaFe$_{12}$O$_{19}$ was observed to have a needle-like microstructure which was not observed in the zero field (ZF) product. After annealing, the coercive field of the AF product was found to be 20% lower than the ZF product. However, no proven explanation for how the magnetic field influenced the reaction was given.

It is desirable to understand how the magnetic field affects the product’s properties, because this offers the potential of tuning the magnetic field to obtain certain, commercially interesting, properties in the product, such as a reduction in coercivity without doping. The aim of the work described in this chapter is to understand how and why magnetic fields influence SHS reactions and products: what happens and why does it happen?

Magnetic fields have been shown to influence gas phase, liquid phase and solid state reactions, as described in Chapter 1. The effect of the field on gaseous combustion was attributed to paramagnetic oxygen being attracted into the magnetic field, thereby promoting combustion. In the liquid phase reactions such as electrodeposition, the field was thought to affect the transport of ions near the cathode, perhaps by the Lorentz force. In solid state SHS reactions on powders, the field was said to act by reorganising the ferromagnetic components of the green mixture along the field lines. The field was also observed to act on compacted powders (pressed pellets) and in this case its influence was attributed to magnetophoresis (reorganisation of the ferromagnetic components as other parts of the green mixture melt as the combustion wave approaches).
The starting point for this work was to characterise the effects of a magnetic field on an SHS reaction and its products. To do this, reactions were performed on barium ferrite green mixture powders in zero field and in a 1.1 T magnetic field. The products from the magnetic field reactions were found to contain two distinct looking parts – shiny and matt regions – which had not previously been noted. These parts were separated and investigated, both post-SHS and after annealing. This investigation led to new experiments on pressed bars of barium ferrite green mixture containing an internal oxidising agent, that were designed to discover the exclusive effects of the magnetic field, by removing variables of shape, density and oxygen diffusivity. Once the effects of the field had been characterised, it was possible to move on to explore why the magnetic field causes those effects. Experiments were performed at a range of field strengths up to 20 T, on strongly magnetic and weakly magnetic systems, to probe the mechanism(s) of how the magnetic field affects SHS reactions.

4.2 Experimental

All the reactions were to form BaFe\textsubscript{12}O\textsubscript{19}. At high magnetic fields reactions were also performed on other systems; these are described in Section 4.2.7. In Sections 4.2.1 to 4.2.5 the reaction temperature was measured by optical pyrometry (and in some cases by thermal imaging camera), and the velocity was found by measuring the length of green mixture and noting the time taken for it to react. The reaction time was defined as the time from ignition to the disappearance of the glow from the bulk of the reacting mixture.

4.2.1 Reactions in zero field

For the zero field reactions, the green mixture was placed inside a quartz tube or on a ceramic mat, as shown in Chapter 2, Figure 2.2, and ignited under a flow of oxygen ca. 2 l min\textsuperscript{-1}. The temperature and velocity of the reaction were measured. The product darkened to brown and became partly fused. A portion of the product was ground and annealed at 1150 °C for 6 hours. The annealed product was a black powder. Both the post-SHS and annealed products were analysed by XRD, VSM and Mössbauer spectroscopy; EDAX and electron microprobe analysis were only performed on the post-SHS samples.
4.2.2 Reactions in a 1.1 T magnetic field

For the magnetic field reactions, the quartz tube was placed inside a 1.1 T permanent magnet Halbach cylinder, with its magnetic axis vertical, as shown in Chapter 2, Figure 2.3. Experiments performed with the axis horizontal showed that the magnetic field axis direction did not significantly affect the appearance of the product, the phase formation or its magnetic properties. The green mixture was attracted into the centre of the magnet and lined up in the magnetic field in an hourglass shape, see Figure 4.1. No separation of the weakly magnetic reactants (BaO$_2$, Fe$_2$O$_3$) was observed, by eye. To check that this was the case, homogeneity experiments were performed at Station 16.4 at Daresbury Laboratory. The white beam of X-rays could be aimed at a particular region of the green mixture inside the magnet. By sampling different spots on the green mixture, along the direction of the magnetic field, the degree of homogeneity of the green mixture was revealed.

The reactions were ignited under a flow of oxygen, ca. 21 min$^{-1}$, and the temperature and velocity were measured. The product was fused and remained in the hourglass shape. It was removed from the magnet by forcing a plunger along the quartz tube. The product had a fibrous appearance, with the direction of the fibres parallel to the applied magnetic field direction. It consisted of two macroscopically distinct looking parts: a fused, shiny, metallic-looking part; and a powdery, brown coloured, matt part. The shiny and matt parts were separated by eye and analysed separately. Portions of the shiny and matt parts were ground and annealed at 1150 °C for 6 hours. The annealed products were black powders. Both the post-SHS and annealed products were analysed by XRD, VSM and Mössbauer spectroscopy; EDAX and electron microprobe analysis were only performed on the post-SHS samples.
1.1 T

Halbach cylinder magnet
Quartz tube
Green mixture

Figure 4.1 – Green mixture in 1.1 T applied magnetic field, adopting an hourglass shape.

4.2.3 Pre-aligned reactions

For the pre-aligned reactions, the green mixture was aligned by a magnetic field, but the field was removed before igniting the reaction. In the pre-aligned set-up, two 25 mm diameter NdFeB magnets, generating a field strength of 0.2 T, were placed either side of the quartz tube (as shown in Chapter 2, Figure 2.4). The mixture aligned along the direction of the field in a “pseudo” hourglass shape, see Figure 4.2. The magnets were removed parallel to the hourglass axis before the green mixture was ignited so that the mixture retained its shape. The reactions were ignited under a flow of oxygen, ca. 21 min⁻¹, and the temperature and velocity were measured. The product was fused and kept its shape. It consisted of shiny fibres and a matt component. The shiny and matt parts were separated and analysed separately. A portion of each part was ground and annealed at 1150 °C for 6 hours. The annealed products were black powders. Both the post-SHS and annealed products were analysed by XRD, VSM and Mössbauer spectroscopy; EDAX and electron microprobe analysis were only performed on the post-SHS samples.
4.2.4 Reactions on powders using perchlorate

Zero field, 1.1 T applied magnetic field and pre-aligned experiments were also performed on powders of barium ferrite green mixture containing sodium perchlorate. The only difference in the way the reactions were performed compared to those just described, was that no oxygen flow was required during the reaction itself, as the perchlorate acts as an internal source of oxygen. The products in all conditions were fused and dark grey/black. A small amount of the applied field product appeared shiny. No fibrous structure was seen in the products as most of the material was thrown to the sides of the tube. The products were crushed and washed with 2 x 100 ml distilled water to remove the co-produced salt, then portions of the product were annealed at 1150 °C for 6 hours. The washed post-SHS and annealed products were analysed by XRD, VSM and Mössbauer spectroscopy; EDAX and electron microprobe analysis were only performed on the post-SHS applied field and pre-aligned powder samples.

4.2.5 Reactions on bars using perchlorate

Bars of 1 g amounts of barium ferrite green mixture containing sodium perchlorate, were pressed to ~100 MPa using a custom built die. The dimensions of the pressed bar were 20 x 5 x 3 mm³. Reactions were performed in both zero field and 1.1 T. Inside the magnet the bar aligned with the field as shown in Figure 4.3, with its long axis parallel to the axis of the quartz tube. No oxygen flow was required as the bars contained perchlorate as an internal oxidising agent.
The zero and applied field products looked identical; both were black, porous, and contained small shiny regions. These were too small to analyse separately. The products were crushed and washed with 2 x 100 ml distilled water to remove the co-produced salt, then portions of the product were annealed at 1200 °C for 2 hours. Electron microprobe analysis was performed on solid pieces of both zero field and applied field reacted bars. The washed post-SHS and annealed products were analysed by XRD, VSM and Mössbauer spectroscopy.

Figure 4.3 – Alignment of pressed bar of green mixture in 1.1 T magnetic field. The long axis of the bar is parallel to the tube axis.

4.2.6 Electrical resistivity measurements

Electrical resistivity measurements were performed at the Royal Institution, London, on an Oxford Instruments Maglab System 2000. The aim of these experiments was to see how the electrical resistivity of the shiny phase of the applied field product varies with temperature, to determine if it is metallic in nature. A piece of post-SHS shiny applied field fused product was investigated. The piece, ~2 x 2 mm², was mounted on a sapphire block within a square chip, and gold wires added to connect the sample to the legs of the chip, Figure 4.4. These connections allowed a current to pass through the sample, and the voltage to be measured across the sample. Using four connections meant that the resistance of the connections was eliminated, so that only the resistance of the sample itself was measured.
Figure 4.4 – Resistivity measurements set-up. The current is supplied via the two outer contacts, and the voltage is measured across the two inner contacts.

The chip was positioned inside the Maglab in a vacuum, which was cooled with liquid helium. The temperature was raised from 50 K to 350 K at a ramp rate of 3 K min⁻¹, with measurements of the resistance (from Ohm’s Law, R=V/I) taken every 0.1 K. Since the resistivity of the sample changed with temperature, the current passed through the contacts had to be altered. The following currents were used: 1 µA for 50-100 K, 100 µA for 100-150 K, 1 mA for 150-300 K and 5 mA for 300-350 K. The resistivity ρ was estimated using Eqn. 4.1,

$$\rho = \frac{AR}{\ell}$$  \hspace{1cm} \text{Eqn. 4.1}

by multiplying the measured resistance R by the estimated cross-sectional area A, and dividing by the estimated distance ℓ between the two voltage contacts. The area A was estimated to be 0.04 cm² and ℓ was estimated to be 0.2 cm. A graph of ln(ρ) vs. 1/T was plotted to determine the electrical conducting nature of the sample and to calculate its band gap.

4.2.7 Experiments at high magnetic field strengths

Experiments were performed in a range of magnetic field strengths, at the High Field Magnet Laboratory at Nijmegen University in March 2001. The aim of these
experiments was to determine why magnetic fields affect SHS reactions, and to achieve this by seeing if there are any trends in the reaction temperature or reaction completeness as a function of field strength. SHS reactions were performed on powders and pellets of various green mixtures, both those containing iron and those containing only paramagnetic and diamagnetic reactants. Reactions were performed on the green mixtures as shown in Table 4.1. The idealised equations are given in Eqn. 4.2 for the formation of strontium titanate and Eqn. 4.3 for barium titanate. The equation for the reaction to form barium ferrite is given in Chapter 2, Eqn. 2.1. Reactions were performed both at zero field and at a range of field strengths up to 20 T.

\[
\begin{align*}
\text{SrO}_2 + 0.3 \text{Ti} + 0.7 \text{TiO}_2 + \text{O}_2 & \rightarrow \text{SrTiO}_3 & \text{Eqn. 4.2} \\
\text{BaO}_2 + 0.3 \text{Ti} + 0.7 \text{TiO}_2 + \text{O}_2 & \rightarrow \text{BaTiO}_3 & \text{Eqn. 4.3}
\end{align*}
\]

Each system shown in Table 4.1 was reacted in field strengths of 0, 5, 10, 15 and 20 T, except the BaFe\textsubscript{12}O\textsubscript{19} powder system which was reacted at 2 T intervals from 0 to 20 T. A higher oxygen flow rate was used for pellets compared to powders, because with compacted samples it is more difficult for oxygen to get into the system. Initially the BaFe\textsubscript{12}O\textsubscript{19} pellets would not ignite, so the molar ratio of fuel to limiter, Fe:Fe\textsubscript{2}O\textsubscript{3} was increased to 8:2. This means that the results for barium ferrite pellets cannot be directly compared with those from the reactions on powders, or those in the lab at UCL, where a 6:3 Fe:Fe\textsubscript{2}O\textsubscript{3} ratio was used.

Table 4.1 – Reactions performed at variable magnetic field strengths at Nijmegen High Field Magnet Laboratory.

<table>
<thead>
<tr>
<th>Pellet / Powder</th>
<th>System</th>
<th>Magnetic description of product</th>
<th>Mass used / g</th>
<th>O₂ flow rate used / 1 min\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>BaTiO\textsubscript{3}</td>
<td>Paramagnetic</td>
<td>~1.4</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>SrTiO\textsubscript{3}</td>
<td>Paramagnetic</td>
<td>~1.4</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>BaFe\textsubscript{12}O\textsubscript{19}</td>
<td>Hard ferrimagnetic</td>
<td>1.5</td>
<td>18</td>
</tr>
<tr>
<td>Powder</td>
<td>SrTiO\textsubscript{3}</td>
<td>Paramagnetic</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>BaFe\textsubscript{12}O\textsubscript{19}</td>
<td>Hard ferrimagnetic</td>
<td>2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a} – green mixture contained 8:2 ratio of Fe:Fe\textsubscript{2}O\textsubscript{3}.
The oxygen flow rates used for the different experiments are shown in Table 4.1. The flow rate measured by the flowmeter is the volume of oxygen output by the cylinder per unit time. The flow rate of oxygen into the reaction region however will depend on the cross-sectional area of the pipe through which it travels – if the area is halved the flow rate will be doubled, for the same flow rate reading on the flowmeter. In the powder set-up the oxygen flowed through a 13 mm diameter pipe, whereas in the pellet set-up the pipe was narrower, only 5 mm diameter. In the lab at UCL a pipe of 15 mm diameter was used. This means that for a 1 l min$^{-1}$ reading on the oxygen flowmeter, the flow rates of oxygen into the reaction regions were 1 l min$^{-1}$ in the UCL lab set-up, 1.3 l min$^{-1}$ in the Nijmegen powder set-up, and 8.8 l min$^{-1}$ in the Nijmegen pellet set-up.

Reactions were performed in a Bitter magnet with a maximum field strength of 20 T. The magnet was 40 cm deep with a 32 mm diameter bore. In the centre of the magnet, the field was uniform to 0.1 % cm$^{-1}$ in both the horizontal and vertical planes. The field direction was vertical, along the axis of the magnet.

Reactions were performed on 13 mm diameter pressed pellets of green mixture, pressed to ~75 MPa and about 2 mm thick. The pellet was placed inside a 30 mm diameter quartz tube and rested on an X-shape of quartz supports, see Figure 4.5. The quartz tube was held in the correct position by some polystyrene spacer blocks, such that the pellet was in the region of maximum, uniform field strength. Oxygen was supplied from the bottom of the tube, with the flow rate measured by a Platon flowmeter. The reactions were ignited by a nichrome wire inserted from the top of the tube. To enable the pellets to ignite, they were smeared with some silicon grease and dipped in titanium powder, as shown in Figure 4.6. By igniting the titanium, enough heat was produced in a small area to allow the SHS reaction to begin. Typically, 12 V and 7 A were required to get the wire hot enough for ignition to occur. After ignition had occurred (this had happened when the wire broke and the current dropped to zero), the field and oxygen flow were left on for about 30 s. The barium ferrite pellets did not stay in the orientation shown in Figure 4.6 – they tended to flip up with their diameters along the magnetic field.
direction. For these reactions the ignition procedure was modified slightly: the pellet (smeared with two blobs of grease + Ti) was placed into the tube, resting on the quartz supports, then the wire was placed into the tube, just above the pellet. The field was switched on, then the hot wire touched onto the pellet.

The reaction temperature was measured by a single diode array spectrometer. Light from the reaction was fed to the spectrometer by an optical fibre, connected to the bottom of the quartz tube. Each spectrum had an exposure time of 3 ms. Spectra were collected at a frequency of 5 spectra per second, over a wavelength range of 500-1150 nm. The reaction temperature was estimated by assuming the reacting pellet was a blackbody radiator, finding the wavelength of maximum spectral emittance and using Wien’s Law to convert the wavelength to temperature, as outlined in Section 4.4.10. The wavelength range of 500-1150 nm is equivalent to a temperature range of 5800 to 2520 K.
Figure 4.5 – Pellet reactions in high magnetic fields up to 20 T at Nijmegen High Field Magnet Laboratory: (a) diagram of experimental set-up in magnet, (b) photograph of quartz tube showing optical fibre and oxygen inlet connections.

Figure 4.6 – Close-up view of pellet ignition for high magnetic field reactions.
Reactions on powders of green mixture were performed inside a specially designed cell, see Figure 4.7, which was loaded with the powder before lowering into the magnet. The cell consisted of a base and a lid, both made of a ceramic material (Al₂O₃) to withstand the high temperatures generated. A photograph is shown in Figure 4.8. The volume inside the cell was approximately 3 cm³. In the bottom of the base was a porous disc of quartz, as an inlet for oxygen supplied via the flowmeter. The lid also contained another porous quartz disc to allow oxygen to flow through the cell, rather than having pressure build up within it. Also, through the lid came the nichrome wire to ignite the reaction. The cell was suspended in position in the magnet by two copper suspension wires, that also functioned as connectors from the ignition wire to the power supply. It was not possible to connect the optical fibre to the powder cell, so no temperature data could be collected for reactions on powders.

**Figure 4.7** – Powder reactions in high magnetic fields up to 20 T at Nijmegen High Field Magnet Laboratory: (a) diagram of experimental set-up in magnet, (b) photograph of powder cell showing suspension wires and oxygen inlet tube.
4.3 Results

The reaction temperatures and velocities are summarised in Table 4.2, along with descriptions of the appearance and microstructure of the products. Photographs of the products and electron microprobe composition maps of the microstructure of selected products are shown in the individual subsections.

The XRD data for the post-SHS and annealed products are given in Table 4.3, which includes the different phases in the post-SHS products in order of abundance, and the lattice parameters of the annealed BaFe$_{12}$O$_{19}$ products. The annealed products were all identified as BaFe$_{12}$O$_{19}$. The lattice parameters of the annealed products are also plotted in Figure 4.9. The $a$ parameters were between 5.883(2) and 5.895(3) Å. These are mostly smaller than the reported values, although none are significantly smaller since they all fall within the ±3σ range. The $c$ parameters were between 23.167(27) and 23.260(12) Å. Most of the $c$ parameters are higher than the reported values, but none are significantly higher. The reported values for the lattice parameters of BaFe$_{12}$O$_{19}$ are $a = 5.892(1)$ to 5.8945(5) Å and $c = 23.183(1)$ to 23.215(3) Å.$^{37,38,39}$ (This does not include the previous reported values for BaFe$_{12}$O$_{19}$ prepared by SHS by the UCL group.$^{69}$)
Table 4.2 – Reaction temperature and velocity and description of products, for reactions performed on barium ferrite green mixture in different conditions.

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Reaction temperature&lt;sup&gt;a&lt;/sup&gt; / °C</th>
<th>Reaction velocity&lt;sup&gt;d&lt;/sup&gt; / mm s&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Product appearance</th>
<th>Amount of shiny phase / %</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaF ZF</td>
<td>975-1000 / 920&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.0</td>
<td>Brown, partially fused powder</td>
<td>0</td>
<td>Homogeneous</td>
</tr>
<tr>
<td>BaF AF</td>
<td>1000-1200 / 1240&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.2-0.25</td>
<td>Brown powdery matt part and shiny, silver coloured part with fused fibrous structure</td>
<td>60-70</td>
<td>Homogeneous (matt)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Needle-like regions (shiny)</td>
</tr>
<tr>
<td>BaF pre-aligned</td>
<td>1150 / 1080&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.2-0.3</td>
<td>Brown powdery matt part and shiny, silver coloured part with fused fibrous structure</td>
<td>30-40</td>
<td>Homogeneous (matt)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Homogeneous (shiny)</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, ZF</td>
<td>1150-1250</td>
<td>1.1-1.4</td>
<td>Dark grey/black, fused, small shiny regions</td>
<td>5-10</td>
<td>Needle-like regions ~20 % coverage</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, AF</td>
<td>1150-1250</td>
<td>0.4-0.7</td>
<td>Dark grey/black, fused, small shiny regions</td>
<td>5-10</td>
<td>Needle-like regions &lt; 5 % coverage</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, pre-aligned</td>
<td>1150-1250</td>
<td>0.5-0.6</td>
<td>Dark grey/black, fused, small shiny regions</td>
<td>5-10</td>
<td>Needle-like regions ~15 % coverage</td>
</tr>
<tr>
<td>BaF + perchlorate, bar, ZF</td>
<td>&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.8</td>
<td>Black, porous, small shiny regions</td>
<td>&lt; 5</td>
<td>Needle-like regions ~15 % coverage</td>
</tr>
<tr>
<td>BaF + perchlorate, bar, AF</td>
<td>&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.8</td>
<td>Black, porous, small shiny regions</td>
<td>&lt; 5</td>
<td>Needle-like regions ~15 % coverage</td>
</tr>
</tbody>
</table>

<sup>a</sup> – Reaction temperature measured by optical pyrometry unless otherwise stated.
<sup>b</sup> – Thermal imaging camera measurements.
<sup>c</sup> – Temperature could not be measured due to excessive smoke produced during the reaction.
<sup>d</sup> – Velocity calculated by measuring length of green mixture and reaction time, from ignition to disappearance of glow from reacting material.
<sup>e</sup> – The microstructure of the ZF perchlorate powder product was not analysed.
Table 4.3 – XRD data for post-SHS and annealed barium ferrite products prepared under different reaction conditions. Products were annealed at 1150 °C for 6 hours or 1200 °C for 2 hours. Products made with perchlorate were also washed prior to analysis.

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Phases identified in post-SHS product, in order of abundance</th>
<th>Phases identified in annealed product</th>
<th>BaFe_{12}O_{19} lattice parameters observed in annealed product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a / \text{Å} ) \hspace{1cm} (c / \text{Å} )</td>
</tr>
<tr>
<td>BaF ZF</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, Fe, Fe_{3}O\textsubscript{4}, Fe_{1+\delta}O, BaFe\textsubscript{2}O\textsubscript{4}, BaO\textsubscript{2}</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{a}</td>
<td>5.889(2) \hspace{1cm} 23.216(7)</td>
</tr>
<tr>
<td>BaF AF matt</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, Fe_{3}O\textsubscript{4}, Fe, BaFe\textsubscript{2}O\textsubscript{4}, Fe_{1+\delta}O, BaO\textsubscript{2}</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{a}</td>
<td>5.889(3) \hspace{1cm} 23.210(10)</td>
</tr>
<tr>
<td>BaF AF shiny</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, BaFe\textsubscript{2}O\textsubscript{4}, Fe_{1+\delta}O, Fe\textsubscript{2}O\textsubscript{4}</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{a}</td>
<td>5.895(3) \hspace{1cm} 23.229(10)</td>
</tr>
<tr>
<td>BaF pre-aligned matt</td>
<td>Fe, Fe\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4}, BaFe\textsubscript{2}O\textsubscript{4}, Fe_{1+\delta}O</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{a}</td>
<td>5.890(3) \hspace{1cm} 23.219(10)</td>
</tr>
<tr>
<td>BaF pre-aligned shiny</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, BaFe\textsubscript{2}O\textsubscript{4}, Fe_{1+\delta}O, Fe\textsubscript{2}O\textsubscript{4}</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{a}</td>
<td>5.894(2) \hspace{1cm} 23.241(7)</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, ZF</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, BaFe\textsubscript{2}O\textsubscript{4}, Fe_{1+\delta}O</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{b}</td>
<td>5.885(2) \hspace{1cm} 23.235(12)</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, AF</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, BaFe\textsubscript{2}O\textsubscript{4}, Fe_{1+\delta}O</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{b}</td>
<td>5.888(3) \hspace{1cm} 23.260(12)</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, pre-aligned</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, BaFe\textsubscript{2}O\textsubscript{4}, Fe_{1+\delta}O</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{b}</td>
<td>5.891(2) \hspace{1cm} 23.235(7)</td>
</tr>
<tr>
<td>BaF + perchlorate, bar, ZF</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, Fe_{1+\delta}O, BaFe\textsubscript{2}O\textsubscript{4}, Fe</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{b}</td>
<td>5.883(2) \hspace{1cm} 23.167(13)</td>
</tr>
<tr>
<td>BaF + perchlorate, bar, AF</td>
<td>Fe\textsubscript{2}O\textsubscript{3}, Fe_{1+\delta}O, Fe, BaFe\textsubscript{2}O\textsubscript{4}</td>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{b}</td>
<td>5.889(4) \hspace{1cm} 23.167(27)</td>
</tr>
<tr>
<td>BaFe\textsubscript{12}O\textsubscript{19} made by ceramic synthesis</td>
<td></td>
<td>BaFe\textsubscript{12}O\textsubscript{19}</td>
<td>5.8996(8) \hspace{1cm} 23.2304(58)</td>
</tr>
<tr>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{37} (PDF#27-1029)</td>
<td></td>
<td>BaFe\textsubscript{12}O\textsubscript{19}</td>
<td>5.892(1) \hspace{1cm} 23.198(1)</td>
</tr>
<tr>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{38} (PDF#39-1433)</td>
<td></td>
<td>BaFe\textsubscript{12}O\textsubscript{19}</td>
<td>5.8945(5) \hspace{1cm} 23.215(3)</td>
</tr>
<tr>
<td>BaFe\textsubscript{12}O\textsubscript{19} \textsuperscript{39} (PDF#43-0002)</td>
<td></td>
<td>BaFe\textsubscript{12}O\textsubscript{19}</td>
<td>5.8920(1) \hspace{1cm} 23.183(1)</td>
</tr>
<tr>
<td>BaFe\textsubscript{12}O\textsubscript{19} previous report by the UCL group \textsuperscript{69}</td>
<td></td>
<td>BaFe\textsubscript{12}O\textsubscript{19}</td>
<td>5.889(1) \hspace{1cm} 23.190(7)</td>
</tr>
</tbody>
</table>

\(a\) – minor phase BaFe\textsubscript{2}O\textsubscript{4} also observed, \(b\) – minor phase Fe\textsubscript{2}O\textsubscript{3} also observed.
Figure 4.9 – Plot of the $a$ and $c$ lattice parameters of the BaFe$_{12}$O$_{19}$ washed and annealed products, grouped into categories related to the synthesis conditions. Also plotted are the literature values for BaFe$_{12}$O$_{19}$. 
Table 4.4 – Mössbauer parameters for post-SHS barium ferrite non-perchlorate products. Isomer shift δ ± 0.01 mm s⁻¹, quadrupole splitting Δ ± 0.02 mm s⁻¹, quadrupole shift 2ε ± 0.02 mm s⁻¹, linewidth Γ ± 0.01 mm s⁻¹, hyperfine field B_{hf} ± 1 kG. Values shown in red were fixed during the fitting process.

<table>
<thead>
<tr>
<th>Fitted phases</th>
<th>ZF</th>
<th>AF matt</th>
<th>AF shiny</th>
<th>Pre-al matt</th>
<th>Pre-al shiny</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>Δ</td>
<td>0.37</td>
<td>0.36</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>2ζ</td>
<td>-0.19</td>
<td>-0.18</td>
<td>-0.06</td>
<td>-0.18</td>
</tr>
<tr>
<td></td>
<td>Γ</td>
<td>0.42</td>
<td>0.29</td>
<td>0.60</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>B_{hf}</td>
<td>522</td>
<td>514</td>
<td>504</td>
<td>514</td>
</tr>
<tr>
<td>Area^a</td>
<td></td>
<td>54.61</td>
<td>26.74</td>
<td>15.93</td>
<td>51.32</td>
</tr>
<tr>
<td>Fe₂O₃₋₁</td>
<td>Δ</td>
<td>0.26</td>
<td>0.27</td>
<td>0.27</td>
<td>0.25</td>
</tr>
<tr>
<td>(tetrahedral sites)</td>
<td>2ζ</td>
<td>0.05</td>
<td>0.00</td>
<td>0.06</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>Γ</td>
<td>0.50</td>
<td>0.26</td>
<td>0.34</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>B_{hf}</td>
<td>492</td>
<td>488</td>
<td>489</td>
<td>487</td>
</tr>
<tr>
<td>Area^a</td>
<td></td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Fe₂O₃₋₂</td>
<td>Δ</td>
<td>0.64</td>
<td>0.65</td>
<td>0.66</td>
<td>0.67</td>
</tr>
<tr>
<td>(octahedral sites)</td>
<td>2ζ</td>
<td>0.06</td>
<td>0.00</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Γ</td>
<td>0.88</td>
<td>0.36</td>
<td>0.45</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>B_{hf}</td>
<td>466</td>
<td>456</td>
<td>461</td>
<td>459</td>
</tr>
<tr>
<td>Area^a</td>
<td></td>
<td>22.80</td>
<td>22.80</td>
<td>22.80</td>
<td>22.80</td>
</tr>
<tr>
<td>BaFe₂O₄</td>
<td>Δ</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>2ζ</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>Γ</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>B_{hf}</td>
<td>471.5</td>
<td>471.5</td>
<td>471.5</td>
<td>471.5</td>
</tr>
<tr>
<td>Area^a</td>
<td></td>
<td>13.78</td>
<td>4.87</td>
<td>10.22</td>
<td>34.53</td>
</tr>
<tr>
<td>Fe₁₋₄O</td>
<td>Δ</td>
<td>0.64</td>
<td>0.83</td>
<td>0.80</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>2ζ</td>
<td>0.64</td>
<td>0.74</td>
<td>0.77</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>Γ</td>
<td>0.88</td>
<td>0.63</td>
<td>0.65</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>B_{hf}</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Area^a</td>
<td></td>
<td>15.50</td>
<td>17.28</td>
<td>13.30</td>
<td>14.25</td>
</tr>
<tr>
<td>Fe</td>
<td>Δ</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>2ζ</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Γ</td>
<td>0.41</td>
<td>0.26</td>
<td>0.30</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>B_{hf}</td>
<td>327</td>
<td>329.5</td>
<td>329.5</td>
<td>330</td>
</tr>
<tr>
<td>Area^a</td>
<td></td>
<td>15.52</td>
<td>5.69</td>
<td>1.07</td>
<td>22.89</td>
</tr>
<tr>
<td>420 kG phase</td>
<td>Δ</td>
<td>0.40</td>
<td>0.43</td>
<td>0.46</td>
<td>0.37</td>
</tr>
<tr>
<td>(uncommon phase)</td>
<td>2ζ</td>
<td>0.10</td>
<td>0.10</td>
<td>0.04</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Γ</td>
<td>0.47</td>
<td>0.28</td>
<td>0.44</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>B_{hf}</td>
<td>420</td>
<td>420</td>
<td>421</td>
<td>420</td>
</tr>
<tr>
<td>Area^a</td>
<td></td>
<td>0.62</td>
<td>2.66</td>
<td>5.81</td>
<td>1.06</td>
</tr>
</tbody>
</table>

^a – Area values are in arbitrary units, relative to one or more sextets with a fixed area value. Because the area values are relative, they can only be compared down a column, within the fits for each particular post-SHS product.
Table 4.5 – Mössbauer parameters for post-SHS barium ferrite perchlorate products. Isomer shift $\delta \pm 0.01$ mm s$^{-1}$, quadrupole splitting $\Delta \pm 0.02$ mm s$^{-1}$, quadrupole shift $2\varepsilon \pm 0.02$ mm s$^{-1}$, linewidth $\Gamma \pm 0.01$ mm s$^{-1}$, hyperfine field $B_{hf} \pm 1$ kG. Values shown in red were fixed during the fitting process.

<table>
<thead>
<tr>
<th>Fitted phases</th>
<th>Post-SHS products</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BaF+per ZF</td>
<td>BaF+per AF</td>
<td>BaF+per pre-al</td>
<td>BaF+per ZF bar</td>
<td>BaF+per AF bar</td>
</tr>
<tr>
<td>Fe$_3$O$_4$-1 (tetrahedral sites)</td>
<td>$\delta$</td>
<td>0.22</td>
<td>0.27</td>
<td>0.26</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>-0.11</td>
<td>0.00</td>
<td>-0.03</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.32</td>
<td>0.27</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>482</td>
<td>488</td>
<td>484</td>
<td>487</td>
</tr>
<tr>
<td></td>
<td>Area$^a$</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Fe$_3$O$_4$-2 (octahedral sites)</td>
<td>$\delta$</td>
<td>0.66</td>
<td>0.65</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>0.01</td>
<td>0.00</td>
<td>-0.04</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.32</td>
<td>0.37</td>
<td>0.33</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>457</td>
<td>455</td>
<td>453</td>
<td>453</td>
</tr>
<tr>
<td></td>
<td>Area$^a$</td>
<td>22.80</td>
<td>22.80</td>
<td>22.80</td>
<td>22.80</td>
</tr>
<tr>
<td>BaFe$_2$O$_4$</td>
<td>$\delta$</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>471.5</td>
<td>471.5</td>
<td>471.5</td>
<td>471.5</td>
</tr>
<tr>
<td></td>
<td>Area$^a$</td>
<td>8.57</td>
<td>5.85</td>
<td>8.42</td>
<td>5.11</td>
</tr>
<tr>
<td>Fe$_{1-x}$O</td>
<td>$\delta$</td>
<td>0.93</td>
<td>0.75</td>
<td>0.89</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>$\Delta$</td>
<td>0.80</td>
<td>0.77</td>
<td>0.78</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.69</td>
<td>0.91</td>
<td>0.70</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Area$^a$</td>
<td>31.72</td>
<td>7.97</td>
<td>12.68</td>
<td>26.72</td>
</tr>
<tr>
<td>Fe</td>
<td>$\delta$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>329.5</td>
<td>329.5</td>
<td>329.5</td>
<td>329.5</td>
</tr>
<tr>
<td></td>
<td>Area$^a$</td>
<td>1.55</td>
<td>1.55</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>420 kG phase (uncommon phase)</td>
<td>$\delta$</td>
<td>0.24</td>
<td>0.35</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>$2\varepsilon$</td>
<td>0.10</td>
<td>0.33</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>0.20</td>
<td>0.28</td>
<td>0.05</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>$B_{hf}$</td>
<td>420</td>
<td>413</td>
<td>421</td>
<td>419</td>
</tr>
<tr>
<td></td>
<td>Area$^a$</td>
<td>1.04</td>
<td>2.33</td>
<td>1.34</td>
<td>2.25</td>
</tr>
</tbody>
</table>

$^a$ - Area values are in arbitrary units, relative to one or more sextets with a fixed area value. Because the area values are relative, they can only be compared down a column, within the fits for each particular post-SHS product.
Table 4.6 – Mössbauer parameters for annealed BaFe$_{12}$O$_{19}$ products, fitted with relative areas in the ratio 12:6:4:1.5. Products were annealed at 1150 °C for 6 hours or 1200 °C for 2 hours. Isomer shift $\delta \pm 0.01$ mm s$^{-1}$, quadrupole shift $2\varepsilon \pm 0.02$ mm s$^{-1}$, linewidth $\Gamma \pm 0.01$ mm s$^{-1}$, hyperfine field $B_{hf} \pm 1$ kG. Values shown in red were fixed during the fitting process.

<table>
<thead>
<tr>
<th>Fe site</th>
<th>Annealed products</th>
<th>ZF</th>
<th>AF matt</th>
<th>AF shiny</th>
<th>Pre-al matt</th>
<th>Pre-al shiny</th>
<th>BaF$^+$ per ZF*</th>
<th>BaF$^+$ per AF*</th>
<th>BaF$^+$ per pre-al*</th>
</tr>
</thead>
<tbody>
<tr>
<td>12k</td>
<td></td>
<td>$\delta$</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.34</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2\varepsilon$</td>
<td>0.40</td>
<td>0.40</td>
<td>0.41</td>
<td>0.42</td>
<td>0.39</td>
<td>0.41</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Gamma$</td>
<td>0.29</td>
<td>0.29</td>
<td>0.30</td>
<td>0.29</td>
<td>0.35</td>
<td>0.28</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{hf}$</td>
<td>413</td>
<td>412</td>
<td>413</td>
<td>410</td>
<td>412</td>
<td>413</td>
<td>412</td>
</tr>
<tr>
<td>4f$_{4}$+2a</td>
<td></td>
<td>$\delta$</td>
<td>0.27</td>
<td>0.27</td>
<td>0.28</td>
<td>0.28</td>
<td>0.26</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2\varepsilon$</td>
<td>0.19</td>
<td>0.20</td>
<td>0.20</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Gamma$</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.36</td>
<td>0.31</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{hf}$</td>
<td>492</td>
<td>491</td>
<td>492</td>
<td>488</td>
<td>490</td>
<td>491</td>
<td>491</td>
</tr>
<tr>
<td>4f$_{6}$</td>
<td></td>
<td>$\delta$</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2\varepsilon$</td>
<td>0.13</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.11</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Gamma$</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{hf}$</td>
<td>514</td>
<td>513</td>
<td>514</td>
<td>514</td>
<td>509</td>
<td>513</td>
<td>514</td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td>$\delta$</td>
<td>0.32</td>
<td>0.33</td>
<td>0.34</td>
<td>0.31</td>
<td>0.32</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2\varepsilon$</td>
<td>2.23</td>
<td>2.24</td>
<td>2.25</td>
<td>2.26</td>
<td>2.22</td>
<td>2.19</td>
<td>2.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Gamma$</td>
<td>0.31</td>
<td>0.29</td>
<td>0.31</td>
<td>0.35</td>
<td>0.32</td>
<td>0.35</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{hf}$</td>
<td>400</td>
<td>399</td>
<td>398</td>
<td>400</td>
<td>398</td>
<td>399</td>
<td>398</td>
</tr>
</tbody>
</table>

* A little Fe$_2$O$_3$ was also identified in these samples.
Figure 4.10 – Plot of the relative areas of each phase within the different post-SHS products, from Mössbauer spectroscopy. The plotting order of the samples is chosen to show the progression in combustion completeness.

Table 4.7 – Magnetic parameters for BaFe$_{12}$O$_{19}$ products made under different reaction conditions, annealed at 1150 °C for 6 hours or 1200 °C for 2 hours. Products made with perchlorate were also washed prior to analysis.

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>$\sigma_{\text{max}}$ / emu g$^{-1}$ (± 0.1)</th>
<th>$\sigma_{\text{rem}}$ / emu g$^{-1}$ (± 0.1)</th>
<th>$H_c$ / Oe (± 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaF ZF</td>
<td>43.1</td>
<td>29.6</td>
<td>2240</td>
</tr>
<tr>
<td>BaF AF matt</td>
<td>43.8</td>
<td>29.8</td>
<td>1980</td>
</tr>
<tr>
<td>BaF AF shiny</td>
<td>43.3</td>
<td>28.7</td>
<td>1590</td>
</tr>
<tr>
<td>BaF AF (shiny + matt)</td>
<td>43.3</td>
<td>28.8</td>
<td>1600</td>
</tr>
<tr>
<td>BaF pre-aligned matt</td>
<td>47.6</td>
<td>32.7</td>
<td>2350</td>
</tr>
<tr>
<td>BaF pre-aligned shiny</td>
<td>55.6</td>
<td>38.8</td>
<td>1820</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, ZF</td>
<td>46.5</td>
<td>30.4</td>
<td>1320</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, AF</td>
<td>49.4</td>
<td>31.2</td>
<td>1230</td>
</tr>
<tr>
<td>BaF + perchlorate, powder, pre-aligned</td>
<td>53.9</td>
<td>34.0</td>
<td>1220</td>
</tr>
<tr>
<td>BaF + perchlorate, bar, ZF</td>
<td>37.2</td>
<td>21.9</td>
<td>1130</td>
</tr>
<tr>
<td>BaF + perchlorate, bar, AF</td>
<td>35.1</td>
<td>20.4</td>
<td>1090</td>
</tr>
</tbody>
</table>
Figure 4.11 – Magnetic hysteresis loops for selected annealed BaFe$_{12}$O$_{19}$ products.

Figure 4.12 – Plot of the measured maximum magnetisation vs. coercive field values for the BaFe$_{12}$O$_{19}$ washed and annealed products, grouped into categories related to the synthesis conditions.
The Mössbauer data for the post-SHS products are given in Table 4.4 (from reactions under a flow of oxygen) and Table 4.5 (from reactions using sodium perchlorate as an internal oxidising agent). The relative areas of the two Fe$_3$O$_4$ components were fixed in the ratio of 1:1.9 for the Fe ions in the A:B sites (tetrahedral:octahedral sites). An area of 1.9 rather than 2 was used due to the difference in recoil free fractions from the two sites. Mössbauer analysis detected the presence of a relatively uncommon iron-containing phase with a hyperfine field of 420 kG. This component was found in all of the post-SHS products regardless of synthesis conditions, and is discussed further in Section 4.4.4. The relative areas of the different phases for each post-SHS product are also plotted in Figure 4.10, which is useful for comparing between the phases in the different products.

The Mössbauer components that were used to fit the annealed products are given in Table 4.6. They were all fitted with four components corresponding to the five different sites for Fe$^{3+}$ in BaFe$_{12}$O$_{19}$, described in Chapter 1, Section 1.3.2. (The components due to the 4f$_4$ and 2a sites were not resolvable.) The 12k, 4f$_4$ + 2a, 4f$_6$ and 2b components were fitted with relative areas in the ratio 12:6:4:1.5 respectively. An area of 1.5 rather than 2 was used for the 2b sites because they have a recoil free fraction that is lower than that for the other sites. No significant differences were seen for the Mössbauer parameters of the annealed products synthesised under different conditions.

VSM measurements of the magnetic properties of the annealed products are given in Table 4.7. Magnetic hysteresis loops for selected products are shown in Figure 4.11 and the maximum magnetisation vs. coercive field values are plotted in Figure 4.12.

4.3.1 Zero field reactions

The zero field reactions of BaO$_2$, Fe and Fe$_2$O$_3$ under a flow of oxygen, had a temperature of 975-1000 °C measured by optical pyrometry, or 920 °C by thermal imaging camera. The velocity was measured as 1.0 mm s$^{-1}$. The product darkened to brown and was partly fused, as shown in Figure 4.13.
Analysis of the post-SHS ZF product by XRD and Mössbauer spectroscopy revealed that it consisted of several phases. In order of abundance these were $\text{Fe}_2\text{O}_3$, Fe, $\text{Fe}_3\text{O}_4$, $\text{Fe}_{1-x}\text{O}$, $\text{BaFe}_2\text{O}_4$ and $\text{BaO}_2$ (determined by XRD and Mössbauer analysis; $\text{BaFe}_2\text{O}_4$ and $\text{BaO}_2$ were only observed by XRD). The results are shown in Table 4.3, Table 4.4 and Figure 4.10. A significant proportion (about 50-60 %, determined by a combination of electron microprobe and Mössbauer analysis) of the post-SHS product was unreacted starting material. Electron microprobe analysis revealed that the post-SHS product had a homogeneous microstructure, as shown in Figure 4.14 (a).

After annealing at 1150 °C for 6 hours the product was a black powder, identified as virtually single phase $\text{BaFe}_{12}\text{O}_{19}$ by XRD and Mössbauer analysis. The lattice parameters were $a = 5.889$ Å and $c = 23.216$ Å, see Table 4.3 and Figure 4.9. The magnetic parameters measured by VSM were $\sigma_{\text{max}} = 43.1$ emu g$^{-1}$, $\sigma_{\text{rem}} = 29.6$ emu g$^{-1}$ and $H_c = 2240$ Oe, see Table 4.7 and Figure 4.12.
4.3.2 1.1 T applied field reactions

The 1.1 T magnetic field reactions of BaO₂, Fe and Fe₂O₃ under a flow of oxygen had a temperature of 1000-1200 °C measured by optical pyrometry, or 1240 °C by thermal imaging camera. The velocity was measured for two runs as 0.2-0.25 mm s⁻¹. The applied field reactions began with a bright glow in the centre of the material, which quickly died away. Photographs of a 1.1 T applied field reaction are shown in Figure 4.15. Careful observation of the video camera footage revealed small fingers of reaction which continued after the main glow had subsided. Video camera recording was used to measure the time taken for the reaction (from ignition to the disappearance of the glowing fingers of reacting material), and hence the velocity.

Figure 4.15 – Photographs of an SHS reaction in a 1.1 T applied magnetic field. The magnetic field direction is vertical and the hourglass shape adopted by the mixture can be seen. Times shown are from the time the reaction was ignited, t = 0 s. The reaction is of BaO₂ + Fe + Fe₂O₃ in an oxygen flow of 2 l min⁻¹. The photographs were taken from video camera footage.
To test the homogeneity of the green mixture in the field, a series of XRD patterns were taken, at Daresbury Station 16.4, where the X-ray beam was positioned at different points on the sample surface. The resultant diffraction patterns were identical, which shows that the green mixture powder does not separate in a magnetic field (at least, not on the scale of the 0.5 mm diameter beam spot).

The product from the applied field reaction was fused and consisted of two macroscopically distinct parts: fused, shiny, fibrous regions and brown coloured, matt regions, see Figure 4.16. The fibres of the shiny parts were aligned along the direction of the applied field. The shiny phase made up about 60-70 % of the applied field product. Breaking up the fused product revealed predominantly grey coloured fibres on the inside, although some of these internal fibres were shiny.

![Image](image_url)

Figure 4.16 – Products from the 1.1 T applied field reaction of BaO$_2$ + Fe + Fe$_2$O$_3$ + oxygen flow: (a) side view, (b) end view, which shows the hourglass shape of the product, (c) internal structure showing predominantly grey fibres. The shiny fibrous macrostructure can be seen in these photographs.

Analysis of the shiny and matt parts of the post-SHS AF product by XRD and Mössbauer spectroscopy revealed that both parts were polyphasic. The results are shown in Table 4.3, Table 4.4 and Figure 4.10. In the matt part six phases were identified; in order of abundance these were Fe$_2$O$_3$, Fe$_3$O$_4$, Fe, BaFe$_2$O$_4$, Fe$_{1-x}$O and BaO$_2$ (determined by XRD and Mössbauer analysis). In the shiny part four phases were identified; in order of abundance these were Fe$_3$O$_4$, BaFe$_2$O$_4$, Fe$_{1-x}$O and Fe$_2$O$_3$. (A little Fe was also observed by Mössbauer analysis). A significant amount of the AF matt part was unreacted starting material (about 50-60 %, determined by a combination of electron microprobe and Mössbauer analysis), whereas in the shiny part less unreacted material was observed (about 30 %). The
composition microstructure of the AF shiny part is shown in Figure 4.14 (b), and shows three distinct regions. These regions were investigated by EDAX spot analysis: needle-like (acicular) shapes of Ba- and Fe-containing phases in a 1:12 ratio, with streaks of Fe or Fe$_2$O$_3$ running through some of them, and BaFe$_2$O$_4$ between the acicular shapes. Initially it was thought that the 1:12 ratio of Ba:Fe might be BaFe$_{12}$O$_{19}$, but Mössbauer and XRD analysis did not reveal the presence of any BaFe$_{12}$O$_{19}$ in the post-SHS products. Some of the particles appear to have texture, but in fact this is porosity in the material. The needle-like microstructure was not observed in the AF matt part, which had a homogeneous microstructure similar to that seen in the ZF product, Figure 4.14 (a). Large area (~100 μm diameter) EDAX scans were performed on the AF shiny and matt parts. These showed similar ratios of Ba to Fe in both parts, indicating that there is no overall segregation of elements.

After annealing the shiny and matt parts at 1150 °C for 6 hours, the products were in both cases a black powder, identified as virtually single phase BaFe$_{12}$O$_{19}$ by XRD and Mössbauer analysis. The lattice parameters were $a = 5.889$ Å, $c = 23.210$ Å for the matt part, and $a = 5.895$ Å, $c = 23.229$ Å for the shiny part, see Table 4.3 and Figure 4.9. The magnetic parameters measured by VSM were $\sigma_{\text{max}} = 43.8$ emu g$^{-1}$, $\sigma_{\text{rem}} = 29.8$ emu g$^{-1}$ and $H_c = 1980$ Oe for the matt part; and $\sigma_{\text{max}} = 43.3$ emu g$^{-1}$, $\sigma_{\text{rem}} = 28.7$ emu g$^{-1}$ and $H_c = 1590$ Oe for the shiny part, see Table 4.7 and Figure 4.12.

An AF product which was not separated into shiny and matt parts before annealing was also measured by VSM. Its magnetic parameters were $\sigma_{\text{max}} = 43.3$ emu g$^{-1}$, $\sigma_{\text{rem}} = 28.8$ emu g$^{-1}$ and $H_c = 1600$ Oe, the same as for the shiny part (within experimental error), see Table 4.7.

4.3.3 Pre-aligned reactions

The pre-aligned reactions of BaO$_2$, Fe and Fe$_2$O$_3$ under a flow of oxygen had a temperature of 1150 °C measured by optical pyrometry, or 1080 °C by thermal imaging camera. The velocity was measured for four runs as 0.2-0.3 mm s$^{-1}$. The
A pre-aligned product was fused, consisting of shiny fibres and a matt component, as shown in Figure 4.17. About 30-40% of the pre-aligned product was shiny. Breaking up the fused pre-aligned product revealed predominantly grey coloured fibres, although some of these internal fibres were shiny.

![Figure 4.17 - Products from the pre-aligned reaction of BaO₂ + Fe + Fe₂O₃ + oxygen flow: (a), (b) side views showing shiny fibrous structure along field direction, (c) end view showing pseudo-hourglass shape, (d) internal structure – mainly grey rather than shiny.](image)

Analysis of the shiny and matt parts of the post-SHS pre-aligned product by XRD and Mössbauer spectroscopy revealed that both parts were polyphasic. The results are shown in Table 4.3, Table 4.4 and Figure 4.10. In the matt part five phases were identified; in order of abundance these were Fe, Fe₂O₃, Fe₅O₄, BaFe₂O₄ and Fe₁₋ₓO (determined by XRD and Mössbauer analysis). In the shiny part the same five phases were identified but in different proportions; in order of abundance these were Fe₃O₄, BaFe₂O₄, Fe₁₋ₓO, Fe₂O₃ and Fe. A significant amount of the pre-aligned matt part was unreacted starting material (about 50-60%, determined by a combination of electron microprobe and Mössbauer analysis), whereas in the shiny part less unreacted material was observed (about 30%). Electron microprobe analysis of the pre-aligned shiny and matt parts showed that both parts had a homogeneous microstructure; no regions of needle-like particles were observed.

After annealing the shiny and matt parts at 1150 °C for 6 hours, the products were in both cases a black powder, identified as virtually single phase BaFe₁₂O₁₉ by XRD and Mössbauer analysis. The lattice parameters were \( a = 5.890 \, \text{Å} \),
\[ c = 23.219 \text{ Å for the matt part, and } a = 5.894 \text{ Å, } c = 23.241 \text{ Å for the shiny part, see Table 4.3 and Figure 4.9. The magnetic parameters measured by VSM were } \sigma_{\text{max}} = 47.6 \text{ emu g}^{-1}, \sigma_{\text{rem}} = 32.7 \text{ emu g}^{-1} \text{ and } H_c = 2350 \text{ Oe for the matt part; and } \sigma_{\text{max}} = 55.6 \text{ emu g}^{-1}, \sigma_{\text{rem}} = 38.8 \text{ emu g}^{-1} \text{ and } H_c = 1820 \text{ Oe for the shiny part, see Table 4.7 and Figure 4.12.}

4.3.4 Zero field reactions on powders using perchlorate

The zero field reactions of BaO\(_2\), Fe, Fe\(_2\)O\(_3\) and NaClO\(_4\) in powder form had a temperature of 1150-1250 °C measured by optical pyrometry. The reaction velocity was measured as 1.1-1.4 mm s\(^{-1}\). The product was dark grey/black and fused, see Figure 4.18. It contained small shiny regions comprising 5-10% of the product. The product was not separated into shiny and matt parts, as had been done for the products from the AF and pre-aligned reactions of BaO\(_2\), Fe and Fe\(_2\)O\(_3\) under a flow of oxygen (i.e. reactions without perchlorate).

Figure 4.18 - Product from the zero field reaction of a powder mixture of BaO\(_2\) + Fe + Fe\(_2\)O\(_3\) + perchlorate.

The post-SHS product was washed, prior to analysis by XRD and Mössbauer spectroscopy. The results are shown in Table 4.3, Table 4.5 and Figure 4.10. Three phases were identified; in order of abundance these were Fe\(_3\)O\(_4\), BaFe\(_2\)O\(_4\) and Fe\(_{1-x}\)O (determined by XRD; a small amount of Fe was also detected by Mössbauer analysis). Unlike the post-SHS products from the reactions without perchlorate, virtually no unreacted starting materials were observed in this post-SHS product.

After annealing at 1150 °C for 6 hours, the product was a black powder, identified as virtually single phase BaFe\(_{12}\)O\(_{19}\) by XRD and Mössbauer analysis. The lattice
parameters were \( a = 5.885 \, \text{Å} \) and \( c = 23.235 \, \text{Å} \), see Table 4.3 and Figure 4.9. The magnetic parameters measured by VSM were \( \sigma_{\text{max}} = 46.5 \, \text{emu g}^{-1} \), \( \sigma_{\text{rem}} = 30.4 \, \text{emu g}^{-1} \) and \( H_c = 1320 \, \text{Oe} \), see Table 4.7 and Figure 4.12.

4.3.5 1.1 T applied field reactions on powders using perchlorate

The 1.1 T applied field reactions of BaO₂, Fe, Fe₂O₃ and NaClO₄ in powder form had a temperature of 1150-1250 °C measured by optical pyrometry. The reaction velocity was measured for two runs as 0.4-0.7 mm s⁻¹. The product was dark grey/black and fused, see Figure 4.19. It contained small shiny regions comprising 5-10% of the product. As for the product from zero field, the AF perchlorate product was not separated into shiny and matt parts.

![Figure 4.19](image_url)

**Figure 4.19 – Product from the 1.1 T applied field reaction of a powder mixture of BaO₂ + Fe + Fe₂O₃ + perchlorate.**

The post-SHS product was washed, prior to analysis by XRD and Mössbauer spectroscopy. The results are shown in Table 4.3, Table 4.5 and Figure 4.10. Three phases were identified; in the same order of abundance as for the ZF product: Fe₅O₄, BaFe₃O₄ and Fe₁₋ₓO (determined by XRD and Mössbauer analysis). Again, no unreacted starting materials were observed. Electron microprobe analysis showed that the post-SHS product contained regions of needle-like particles, similar to the microstructure shown in Figure 4.14 (b). The needle-like particles covered about 20% of the sample area.

After annealing the AF product at 1150 °C for 6 hours, the product was a black powder, identified as virtually single phase BaFe₁₂O₁₉ by XRD and Mössbauer analysis. The lattice parameters were \( a = 5.888 \, \text{Å} \) and \( c = 23.260 \, \text{Å} \), see Table 4.3 and Figure 4.9. The magnetic parameters measured by VSM were
\[ \sigma_{\text{max}} = 49.4 \text{ emu g}^{-1}, \sigma_{\text{rem}} = 31.2 \text{ emu g}^{-1} \text{ and } H_c = 1230 \text{ Oe}, \text{ see Table 4.7 and Figure 4.12.} \]

4.3.6 Pre-aligned reactions on powders using perchlorate

The pre-aligned reactions of \( \text{BaO}_2, \text{Fe, Fe}_2\text{O}_3 \) and \( \text{NaClO}_4 \) in powder form had a temperature of 1150-1250 °C measured by optical pyrometry. The reaction velocity was measured for two runs as 0.5-0.6 mm s\(^{-1}\). The product was dark grey/black and fused and looked similar to the product from the AF reaction, Figure 4.19. It contained small shiny regions comprising 5-10 % of the product. As for the ZF and AF products, the pre-aligned perchlorate product was not separated into shiny and matt parts.

The post-SHS product was washed, prior to analysis by XRD and Mössbauer spectroscopy. The results are shown in Table 4.3, Table 4.5 and Figure 4.10. Three phases were identified; in the same order of abundance as for the ZF and AF products: \( \text{Fe}_2\text{O}_4, \text{BaFe}_2\text{O}_4 \) and \( \text{Fe}_{1-x}\text{O} \) (determined by XRD and Mössbauer analysis). Again, no unreacted starting materials were observed. Electron microprobe analysis showed that the post-SHS product had a predominantly homogeneous microstructure. Some needle-like regions were observed with a coverage of less than 5 % of the sample area.

After annealing the pre-aligned product at 1150 °C for 6 hours, the product was a black powder, identified as virtually single phase \( \text{BaFe}_{12}\text{O}_{19} \) by XRD and Mössbauer analysis. The lattice parameters were \( a = 5.891 \text{ Å} \) and \( c = 23.235 \text{ Å} \), see Table 4.3 and Figure 4.9. The magnetic parameters measured by VSM were \( \sigma_{\text{max}} = 53.9 \text{ emu g}^{-1}, \sigma_{\text{rem}} = 34.0 \text{ emu g}^{-1} \text{ and } H_c = 1220 \text{ Oe}, \text{ see Table 4.7 and Figure 4.12.} \)

4.3.7 Zero field reactions on pressed bar using perchlorate

Zero field reactions of \( \text{BaO}_2, \text{Fe, Fe}_2\text{O}_3 \) and \( \text{NaClO}_4 \) were also performed on the green mixture pressed into a rectangular bar. The reaction temperature could not be measured due to experimental difficulties (smoke was produced). The reaction velocity was measured as 0.8 mm s\(^{-1}\). The product was black, porous, and
contained small shiny regions, comprising < 5 % of the product, see Figure 4.20. The shiny regions were too small to be separated.

Figure 4.20 – Product from the zero field reaction of a pressed bar of \( \text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 + \text{perchlorate} \).

The post-SHS product was washed, prior to analysis by XRD and Mössbauer spectroscopy. The results are shown in Table 4.3, Table 4.5 and Figure 4.10. Four phases were identified; in order of abundance these were \( \text{Fe}_3\text{O}_4, \text{Fe}_{1-x}\text{O}, \text{BaFe}_2\text{O}_4 \) and Fe (determined by XRD and Mössbauer analysis). Unlike the post-SHS products from the powder reactions with perchlorate, the ZF post-SHS perchlorate bar product contained a little unreacted starting material (about 5-10 %, determined by a combination of electron microprobe and Mössbauer analysis). Electron microprobe analysis of an unwashed piece of the post-SHS ZF bar product revealed an acicular microstructure, Figure 4.21 (a). The needle-like particles covered about 15 % of the sample area.

Figure 4.21 – Electron microprobe composition maps of the microstructures of the post-SHS products from the reaction of pressed bars of \( \text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 + \text{perchlorate} \) in (a) zero field, (b) 1.1 T applied field.
After annealing the powdered and washed 2T bar product at 1200 °C for 2 hours, the product was a black powder, identified as virtually single phase BaFe\textsubscript{12}O\textsubscript{19} by XRD and Mössbauer analysis. The lattice parameters were $a = 5.883$ Å and $c = 23.167$ Å, see Table 4.3 and Figure 4.9. The magnetic parameters measured by VSM were $\sigma_{\text{max}} = 37.2$ emu g\textsuperscript{-1}, $\sigma_{\text{rem}} = 21.9$ emu g\textsuperscript{-1} and $H_c = 1130$ Oe, see Table 4.7 and Figure 4.12.

4.3.8 1.1 T applied field reactions on pressed bar using perchlorate

1.1 T applied field reactions of BaO\textsubscript{2}, Fe, Fe\textsubscript{2}O\textsubscript{3} and NaClO\textsubscript{4} were also performed on the green mixture pressed into a rectangular bar. As for the reactions on the bar in zero field, the reaction temperature could not be measured. The reaction velocity was measured as 0.8 mm s\textsuperscript{-1}. The product looked identical to the product in zero field; it was black, porous, and contained small shiny regions, comprising < 5 % of the product. The shiny regions were too small to be separated.

The post-SHS product was washed, prior to analysis by XRD and Mössbauer spectroscopy. The results are shown in Table 4.3, Table 4.5 and Figure 4.10. The same four phases as for the ZF bar product were identified, but in slightly different proportions. In order of abundance these were Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{1-x}O, Fe and BaFe\textsubscript{2}O\textsubscript{4} (determined by XRD and Mössbauer analysis). Again, unlike the post-SHS products from the powder reactions with perchlorate, the AF post-SHS perchlorate bar product contained a little unreacted starting material (about 5-10 %, determined by a combination of electron microprobe and Mössbauer analysis). Electron microprobe analysis of an unwashed piece of the post-SHS AF bar product revealed an acicular microstructure, Figure 4.21 (b), as was observed for the ZF bar product. The needle-like particles covered about 15 % of the sample area.

After annealing the powdered and washed AF bar product at 1200 °C for 2 hours, the product was a black powder, identified as virtually single phase BaFe\textsubscript{12}O\textsubscript{19} by XRD and Mössbauer analysis. The lattice parameters were $a = 5.889$ Å and $c = 23.167$ Å, see Table 4.3 and Figure 4.9. The magnetic parameters measured by
VSM were $\sigma_{\text{max}} = 35.1 \text{ emu g}^{-1}$, $\sigma_{\text{rem}} = 20.4 \text{ emu g}^{-1}$ and $H_c = 1090 \text{ Oe}$, see Table 4.7 and Figure 4.12.

4.3.9 Electrical resistivity measurements

Electrical resistivity measurements of the shiny part of an AF post-SHS product are shown in Figure 4.22. The resistivity was found to decrease with increasing temperature, which is typical for semiconducting or insulating behaviour. A transition was noticed at $\sim 120 \text{ K}$. This is the Verwey transition for magnetite, Fe$_3$O$_4$. Above the Verwey transition temperature magnetite behaves like a poor metal, but below this temperature it distorts to a semiconducting phase of lower symmetry. The band gap of the sample was calculated using Eqn. 4.4,

$$\sigma = Ae^{\frac{-E_g}{kT}}$$

Eqn. 4.4

where $\sigma$ = conductivity, $A$ = constant, $E_g$ = band gap, $k$ = Boltzmann's constant and $T$ = temperature. Taking the natural logarithm gives Eqn. 4.5,

$$\ln \sigma = \ln A - \frac{E_g}{kT}$$

Eqn. 4.5

and since $\sigma = 1/\rho$,

$$\ln \rho = -\ln A + \frac{E_g}{kT}.$$  

Eqn. 4.6

From Eqn. 4.6 it can be seen that the gradient on a $\ln \rho$ vs. $1/T$ graph is $+E_g/k$. The band gaps were measured by calculating the gradient of the $\ln \rho$ vs. $1/T$ curve above and below the transition temperature; values of $E_g = 66 \text{ meV}$ for $T > 120 \text{ K}$ (poor-metal behaviour region) and $E_g = 76 \text{ meV}$ for $T < 100 \text{ K}$ (semiconductor behaviour region) were found.
Figure 4.22 – Plot of ln (resistivity) vs. 1/temperature for a shiny piece of a barium ferrite post-SHS product. The lines in red are extrapolations to determine the gradient.

4.3.10 Experiments at high magnetic field strengths

Reactions were performed on barium ferrite, barium titanate and strontium titanate green mixtures, in pellet and powder form, in a range of magnetic field strengths up to 20 T. It should be remembered that the green mixtures for the barium ferrite pellet reactions used an 8:2 ratio of Fe fuel to Fe₂O₃ limiter, so comparisons with the results for powders or those from the lab at UCL must be treated with care.

The barium ferrite pellet products were very shiny – no matt parts were observed at any field strength. Photographs of the products reacted in different field strengths are shown in Figure 4.23. The pellet products were curved, highly reflective, a dark silver colour, and generally remained in one piece. The internal structure of a pellet is shown in Figure 4.24; it is porous with a dark silver colour and a metallic lustre.
Figure 4.23 – Barium ferrite post-SHS products from pellets reacted in magnetic field strengths of 0, 5, 10, 15 and 20 T.

Figure 4.24 – Internal structure of a barium ferrite pellet reacted at 15 T.

The barium ferrite powder products are shown in Figure 4.25. Below 10 T the products were globular, but at 10 T and higher field strengths the powder had gone to the edges of the reaction cell and took up a ring shape. The products were fused and shiny, and contained some matt parts. For analysis purposes the complete products were ground up (i.e. shiny and matt parts were not separated).
Figure 4.25 – Barium ferrite post-SHS products from powders reacted in magnetic field strengths from 0 to 20 T.

As well as reactions on the strongly magnetic system, BaFe_{12}O_{19}, reactions on the weakly magnetic SrTiO_3 and BaTiO_3 systems were performed at Nijmegen in a range of field strengths. This was to aid our understanding of why magnetic fields affect SHS reactions.

The strontium titanate pellet products are shown in Figure 4.26. At 5 and 10 T the products were in several pieces, but at the other field strengths they remained whole. They appeared as if they had melted and expanded during the reaction.
Figure 4.26 – Strontium titanate post-SHS products from pellets reacted in magnetic field strengths of 0, 5, 10, 15 and 20 T.

The strontium titanate powder products were partly fused and did not take up any particular shape within the reaction cell. The barium titanate pellet products (photographs not shown) looked similar to the reacted strontium titanate products shown in Figure 4.26.

The data recorded by the spectrometer is shown in Figure 4.27 and Figure 4.28 which are plots of intensity vs. wavelength for reactions on BaFe$_{12}$O$_{19}$ and BaTiO$_3$ pellets, respectively. The spectra are overlaid; each spectrum shows the light emitted by the reaction at a particular moment, and as time progresses the peak intensity at first increases then decreases. Two peaks were observed: the peak at the shorter wavelength (higher temperature) was attributed to the ignition of the titanium powder, while the peak at the longer wavelength (lower temperature) was assumed to correspond to the SHS reaction of the pellet.
Figure 4.27 – Spectrometer data (intensity vs. wavelength) from the reaction of a pellet to form barium ferrite in different magnetic field strengths: (a) 0 T, (b) 5 T, (c) 10 T, (d) 15 T and (e) 20 T. The spectra collected at different time intervals are overlaid.
Figure 4.28 – Spectrometer data (intensity vs. wavelength) from the reaction of a pellet to form barium titanate in different magnetic field strengths: (a) 0 T, (b) 5 T. The spectra collected at different time intervals are overlaid.

Plots of the reaction-peak wavelength vs. time and its normalised intensity vs. time, for reactions on BaFe$_{12}$O$_{19}$ and BaTiO$_3$ pellets, are shown in Figure 4.29. The peak wavelength of the light emitted from the reacting pellet is inversely related to the reaction temperature; it is plotted against time in Figure 4.29 (a) for BaFe$_{12}$O$_{19}$ and (c) for BaTiO$_3$. The intensity is a measure of the light emitted by the reacting pellet, and is plotted against time in Figure 4.29 (b) for BaFe$_{12}$O$_{19}$ and (d) for BaTiO$_3$. The data presented in these plots is useful to compare how a magnetic field influences SHS reactions on both weakly and strongly magnetic systems.

Data is not presented for all ten runs which were recorded, because not every run gave extractable peaks due to overloading of the spectrometer. No data is presented for the reactions on the SrTiO$_3$ pellets because all five of those runs overloaded the spectrometer. The spectrometer could collect a maximum of 4000 counts per channel; if the amount of incident light registered exceeded 4000 counts then a peak was not recorded. The spectrometer began collecting data before the reaction was ignited. The time $t = 0$ s in Figure 4.29 was chosen to be the time at which the intensity of the reaction peak was a maximum.
Figure 4.29 – Plots of the spectrometer data from the Nijmegen high magnetic field reactions on pellets of: (a), (b) BaFe\textsubscript{12}O\textsubscript{19} and (c), (d) BaTiO\textsubscript{3}. The wavelength of the peak attributed to the SHS reaction is plotted vs. time in (a) and (c); the normalised intensity of this peak is plotted vs. time in (b) and (d).
The post-SHS products from the SrTiO$_3$ and BaFe$_{12}$O$_{19}$ pellet and powder reactions were analysed by X-ray diffraction. The SrTiO$_3$ reactions essentially went to completion at all magnetic field strengths; the products from the pellet reactions were single phase SrTiO$_3$, whereas the products from the reactions on powders also contained a small amount of the starting materials SrO$_2$ and TiO$_2$. Lattice parameters for the post-SHS SrTiO$_3$ products ranged from $a = 3.9037(13)$ to $3.9078(6)$ Å; the literature value for SrTiO$_3$ is 3.9050 Å. The BaFe$_{12}$O$_{19}$ reactions did not go to completion at any magnetic field strength, in either the pellets or powders. The phases identified in the barium ferrite pellet and powder products are shown in Table 4.8.

Table 4.8 – Approximate phase composition (volume %) of post-SHS products from BaFe$_{12}$O$_{19}$ reactions at different magnetic field strengths up to 20 T, determined by X-ray diffraction.

<table>
<thead>
<tr>
<th>Field / T</th>
<th>Fe$_3$O$_4$</th>
<th>BaFe$_2$O$_4$</th>
<th>Fe$_2$O$_3$</th>
<th>Fe$_{1-x}$O</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Powder</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>50 %</td>
<td>40 %</td>
<td>-</td>
<td>10 %</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>50 %</td>
<td>40 %</td>
<td>5 %</td>
<td>5 %</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>45 %</td>
<td>30 %</td>
<td>10 %</td>
<td>10 %</td>
<td>5 %</td>
</tr>
<tr>
<td><strong>Pellet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>70 %</td>
<td>15 %</td>
<td>5 %</td>
<td>-</td>
<td>10 %</td>
</tr>
<tr>
<td>10</td>
<td>50 %</td>
<td>40 %</td>
<td>-</td>
<td>5 %</td>
<td>5 %</td>
</tr>
<tr>
<td>20</td>
<td>60 %</td>
<td>25 %</td>
<td>-</td>
<td>10 %</td>
<td>5 %</td>
</tr>
</tbody>
</table>

- denotes phases that were not observed.

The post-SHS products from the BaFe$_{12}$O$_{19}$ pellet and powder reactions were analysed by VSM. The results are given in Table 4.9. The maximum magnetisation and remanent magnetisation of the powder products were found to decrease with increasing field strength. No such trend was observed in the pellet parameters. The coercive field values are an order of magnitude smaller than for the annealed products; this is because the hexagonal ferrite phase is not formed in the post-SHS products.
Table 4.9 – Magnetic parameters for post-SHS products from BaFe_{12}O_{19} reactions on powders and pellets at different magnetic field strengths up to 20 T.

<table>
<thead>
<tr>
<th>Magnetic field strength / T</th>
<th>$\sigma_{\text{max}} / \text{emu g}^{-1}$ (±0.1)</th>
<th>$\sigma_{\text{rem}} / \text{emu g}^{-1}$ (±0.1)</th>
<th>$H_r / \text{Oe}$ (± 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Powder</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>58.2</td>
<td>13.1</td>
<td>130</td>
</tr>
<tr>
<td>4</td>
<td>56.1</td>
<td>12.8</td>
<td>160</td>
</tr>
<tr>
<td>10</td>
<td>54.7</td>
<td>11.5</td>
<td>120</td>
</tr>
<tr>
<td>14</td>
<td>52.3</td>
<td>10.4</td>
<td>130</td>
</tr>
<tr>
<td>20</td>
<td>50.2</td>
<td>9.8</td>
<td>140</td>
</tr>
<tr>
<td><strong>Pellet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>57.8</td>
<td>12.9</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>59.7</td>
<td>13.0</td>
<td>130</td>
</tr>
<tr>
<td>10</td>
<td>56.1</td>
<td>11.0</td>
<td>130</td>
</tr>
<tr>
<td>15</td>
<td>58.8</td>
<td>11.7</td>
<td>130</td>
</tr>
<tr>
<td>20</td>
<td>58.9</td>
<td>12.1</td>
<td>130</td>
</tr>
</tbody>
</table>

4.4 **Analysis and Discussion**

The aim of the work described in this chapter was to characterise what happens when SHS is performed in a magnetic field, and to attempt to understand the mechanisms behind the influence of the field. There were several questions to address about the effect of a magnetic field, some of which were there at the start of this project, while others arose from results obtained during the course of the investigations. For example, must the magnetic field be applied during the reaction in order to observe an effect, or is it just the alignment of the green mixture in the field that is important? What are the exclusive effects of the applied field when other factors such as shape, density and oxygen accessibility are taken into account? Why does a magnetic field make the reactions hotter and change the magnetic properties of the products? What is the nature of the shiny parts observed in the applied field and pre-aligned reactions? Why is a needle-like microstructure formed in some of the products?
In the following sections, various aspects of the results will be discussed. The reaction temperatures and velocities shed light on the influence of the magnetic field on the reactions themselves, and it is interesting to relate this to the Curie temperatures of the materials involved. The nature of the shiny parts leads to a discussion of the reaction completeness and possible reaction pathways, which also has a bearing on the unidentified 420 kG Mössbauer component that was observed. The needle-like microstructure of the post-SHS products and the reduction in coercive field of the annealed products are discussed. Pre-aligned reactions began to address the issue of the mechanism of the magnetic field effects. Experiments with perchlorate are discussed in terms of how they help us to determine the exclusive effects of the magnetic field. Electrical resistivity measurements relate to the nature of the shiny parts of the products. The experiments at high magnetic fields addressed ideas about the mechanism of how the magnetic field influences the reactions.

4.4.1 Temperatures and velocities

The reactions on non-perchlorate barium ferrite powders were found to be hotter in AF compared to ZF: 1000-1200 °C vs. 975-1000 °C. The applied field reactions were also found to be faster – this can be seen from the results presented in Chapter 3, Table 3.6, where the reaction times for equal masses of green mixtures are compared. Comparing the time taken for equal masses of green mixture to react was found to provide a more meaningful measure of the reaction velocity, than measurements of the length of green mixture and time taken to react. As discussed in Chapter 3, Section 3.4.4, the velocities quoted in mm s^{-1} should be treated with caution because equal masses of green mixture in ZF and AF are likely to have different lengths and densities. (The velocities quoted in this chapter are in mm s^{-1}; equal mass measurements would have been better, but they were not performed.) Also, the propagation wave travels both along and down into the green mixture at different rates, which makes velocity in mm s^{-1} less meaningful. The fact that a range of velocities were noted for the AF and pre-aligned reactions suggests some variability in these reactions.
The magnetic field was not observed to influence the temperature of reactions on perchlorate-containing barium ferrite powders and bars; temperatures of 1150-1250 °C were measured in ZF, AF and pre-aligned reactions. The field may not affect these reactions because the effect of the improved oxygen flow due to the perchlorate could be much greater than the effect of the field. Alternatively, the reactions may have reached their maximum temperature so that the field is unable to cause any further increase. The results given in Table 4.2 suggest that the reactions were faster when perchlorate was used as an internal oxidising agent, compared to reactions in an external flow of oxygen. The velocities of the reactions on perchlorate-containing powders were measured to be lower in the AF and pre-aligned arrangements, compared to ZF, in a similar way to the non-perchlorate powders. It must be remembered that the velocities quoted in mm s\(^{-1}\) should be treated with caution (for the reasons discussed above).

For all of the reactions, the measured temperature exceeds the Curie temperatures of the ferromagnetic or ferrimagnetic reactants and products, shown in Table 4.10. The relationship between the size of the magnetic field effect and the Curie and reaction (combustion) temperatures, as reported in the literature, was discussed in Chapter 1, Section 1.5.3. Below the Curie temperature, the magnetic field can act by the ferro- or ferri-magnetic components aligning along the field lines. Above the Curie temperature the phases are only weakly magnetic (paramagnetic) so the action of the field is likely to have only a tiny effect by alignment of the now weakly magnetic components. However, the field may be acting by other mechanisms above the Curie temperature, for example, it may act on ions in molten phases in the reaction zone. Magnetic fields were seen to influence liquid phase reactions, for example the electrodeposition of diamagnetic copper discussed in Chapter 1, Section 1.4.2.
Table 4.10 – Curie temperatures for phases involved in SHS reactions to form BaFe$_{12}$O$_{19}$ (from Landolt-Börnstein$^{32}$ and Handbook of Chemistry and Physics$^{33}$).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Curie temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaFe$<em>{12}$O$</em>{19}$</td>
<td>450</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>577</td>
</tr>
<tr>
<td>Fe</td>
<td>820</td>
</tr>
</tbody>
</table>

4.4.2 Shiny and matt parts / Reaction completeness

Shiny and matt parts were observed in some of the products (see Table 4.2) although this had not been reported by previous researchers. Shiny parts form primarily in reactions on powders in magnetic fields. They can also form in zero field when a large mass of sample is used, and in zero field or with pre-aligned powder when a large oxygen flow rate is used. Results presented in Chapter 3 showed that the amount of shiny part increased with increasing oxygen flow rate. Magnetic fields and higher oxygen flow rates are associated with higher reaction temperatures. The formation of shiny parts therefore seems to be due to increased reaction temperatures.

An applied magnetic field leads to a greater degree of conversion of the reactants to the products. The shiny part of the AF product was found to be more fully combusted than the matt part or the ZF product. About 30% of the shiny part of the applied field product was unreacted starting material, compared with about 50-60% of the zero field product. The better degree of conversion in the AF product is related to the higher temperatures reached in the reaction, ca. 1200 °C in applied field compared with 1000 °C in zero field. The shiny part of the applied field product contained more of the combusted products Fe$_3$O$_4$ and BaFe$_2$O$_4$ than the product from zero field, as shown in Table 4.3 and Figure 4.10. By comparing with the proposed reaction scheme for BaFe$_{12}$O$_{19}$, Figure 4.30, it can be seen that Fe$_3$O$_4$ and BaFe$_2$O$_4$ are intermediates on the way to the final BaFe$_{12}$O$_{19}$ product. So, the reaction goes further towards completion in a magnetic field.
Figure 4.30 – Reaction scheme for the reaction of BaO₂ + Fe + Fe₂O₃ + O₂ to form BaFe₁₂O₁₉. Phases identified in the post-SHS products are shown in boxes (BaO falls below the detection limits of the equipment used).

The AF and pre-aligned products were manually separated into shiny and matt parts. This separation process is not perfect and can lead to errors when comparing the relationships between shiny and matt parts for the different products.

There is still the question of why the shiny part is shiny. It may be a surface glazing effect, or it may be due to the metallic nature of the material present (this aspect is discussed in Section 4.4.9). A glaze is a glass-like surface coating applied to ceramic materials. The shininess of the AF and pre-aligned products is not confined to the surface. Their internal structure is predominantly grey/black, but does contain shiny fibres. The powder in the magnetic field separates into fibres which are not too densely packed; i.e. it is reasonable to say that even the internal fibres are shiny due to surface glazing (it is the surfaces of those fibres that are shiny).
4.4.3 Reaction chemistry

Figure 4.30 describes the probable reaction pathways in the reaction of \( \text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 + \text{O}_2 \) to form \( \text{BaFe}_{12}\text{O}_{19} \). Iron in the presence of oxygen will be oxidised, forming wüstite, \( \text{Fe}_{1-x}\text{O} \). The iron in this phase is mostly \( \text{Fe}^{2+} \), though some \( \text{Fe}^{3+} \) will be present to maintain charge neutrality. In \( \text{Fe}_{1-x}\text{O} \), \( x \) may take values from 0.02 to 0.167.\(^7\) (The \( x \) value in the \( \text{Fe}_{1-x}\text{O} \) phases identified in the barium ferrite post-SHS samples could not be determined due to insufficient quality of the XRD data.) Wüstite may be further oxidised to form magnetite, \( \text{Fe}_3\text{O}_4 \), by combining with oxygen or with \( \text{Fe}_2\text{O}_3 \). Also, wüstite may be oxidised to form \( \text{Fe}_2\text{O}_3 \) with all the iron in the \( \text{Fe}^{3+} \) state. Iron oxide, \( \text{Fe}_2\text{O}_3 \), was also one of the starting materials. It may be reduced by combining with \( \text{Fe}_{1-x}\text{O} \) to form \( \text{Fe}_3\text{O}_4 \), which would then be oxidised in the presence of oxygen to re-form \( \text{Fe}_2\text{O}_3 \). Barium peroxide decomposes at 800 °C\(^3\) which releases oxygen and leaves \( \text{BaO} \), although \( \text{BaO} \) has not been isolated in the post-SHS products. This is likely to combine with \( \text{Fe}_2\text{O}_3 \) to form barium monoferrite, \( \text{BaFe}_2\text{O}_4 \).

In the post-SHS products the following phases have been identified: \( \text{Fe}_{1-x}\text{O} \), \( \text{Fe}_3\text{O}_4 \), \( \text{Fe}_2\text{O}_3 \) and \( \text{BaFe}_2\text{O}_4 \). These phases then combine during the annealing stage to form the hexagonal ferrite \( \text{BaFe}_{12}\text{O}_{19} \). The hexagonal M-type structure is composed of hexagonal R blocks and cubic spinel S blocks, as described in Chapter 1, Section 1.3.2. The hexagonal R block has the composition \((\text{BaFe}_6\text{O}_{11})^{2-31}\) which is perhaps formed by \( \text{BaFe}_2\text{O}_4 \) combining with \( \text{Fe}_3\text{O}_4 \) and/or \( \text{Fe}_2\text{O}_3 \). The spinel S block has the composition \((\text{Fe}_6\text{O}_8)^{2+\text{r}}\)\(^9\). It is likely that this block is formed by two \( \text{Fe}_3\text{O}_4 \) units (\( \text{Fe}_3\text{O}_4 \) has a spinel structure).

4.4.4 420 kG Mössbauer component

In the Mössbauer fitting process a component with a hyperfine field, \( B_{hf} \), of \(~420 \text{ kG} \) was required to fit all of the barium ferrite post-SHS products. The identity of the phase that this corresponds to is not immediately known. XRD data does not help to identify this phase, so it may be an Fe-containing phase that is amorphous, or a phase that is structurally indistinguishable from \( \text{Fe} \), \( \text{Fe}_2\text{O}_3 \), \( \text{Fe}_3\text{O}_4 \), \( \text{Fe}_{1-x}\text{O} \) or \( \text{BaFe}_2\text{O}_4 \). The other Mössbauer parameters for this component are
\[ \delta = 0.4 \text{ mm s}^{-1}, \ 2\epsilon = 0.1 \text{ mm s}^{-1} \ \text{and} \ \Gamma = 0.05-0.47 \text{ mm s}^{-1}. \]

This phase may be something like BaFe\textsubscript{6}O\textsubscript{11}, postulated as a phase formed in the annealing process from the post-SHS to the annealed BaFe\textsubscript{12}O\textsubscript{19} product. It may be that during the SHS reaction some BaFe\textsubscript{2}O\textsubscript{4} combines with the iron oxide phases present to produce an intermediate phase, such as BaFe\textsubscript{6}O\textsubscript{11}, that is on the way to BaFe\textsubscript{12}O\textsubscript{19}.

### 4.4.5 Needle-like microstructure

A needle-like microstructure was observed in all the barium ferrite + perchlorate products that were analysed: AF and pre-aligned powder products, and ZF and AF bar products. When perchlorate was not used, only the shiny part of the AF product had a needle-like microstructure, see Table 4.2, Figure 4.14 and Figure 4.21. Magnetic fields and the use of sodium perchlorate are both associated with higher reaction temperatures. It therefore seems reasonable that the needle-like microstructure forms due to higher temperatures reached in the reaction.

The needle-like microstructure was observed for reactions on both powders and bars. The needle shapes were not aligned in any specific direction to each other, i.e. they did not all align parallel to the magnetic field. This suggests that the formation of this microstructure is not related to the reorganisation of the material along the magnetic field lines.

The needle shapes have a 1:12 ratio of Ba:Fe, but they are not BaFe\textsubscript{12}O\textsubscript{19}. Instead they may be intimate mixtures of BaFe\textsubscript{2}O\textsubscript{4} and Fe\textsubscript{3}O\textsubscript{4}, or microcrystals (which could be tested by electron diffraction). The existence of these needle shapes suggests a better degree of combustion compared to products with a finer scale homogeneous microstructure. The formation of the needle shapes thus has links with other reported results, described in Chapter 1, Section 1.5.1. Magnetic field synthesis (on pellets) led to more complete combustion with larger regions of each phase in the product structure, and this was attributed to the phenomenon of magnetophoresis. Magnetophoresis is where charged particles in a fluid move under the influence of a magnetic field, and the liquid and solid phases separate. So perhaps the formation of needle shapes is due to magnetophoresis, although it cannot explain why needle shapes are observed in the absence of a field (ZF...
perchlorate products). Needle-shapes are associated with higher reaction temperatures – it may be that higher temperatures lead to a greater proportion of liquid phase, and better mobility of the solid phases to form the needle shapes. Some star shapes were observed in the microstructure photographs, Figure 4.14 (b), which suggests that the needle shapes may reveal the reaction pathways. The reaction may nucleate at the centre of the star and spread out from there. Percolation effects may also be involved in the needle-shape formation. For the reaction to occur the right materials must be present and close enough to react. The reason that the needle shapes form therefore remains open to speculation.

4.4.6 Magnetic properties of the products

The annealed shiny part of the AF product was found to have a reduced coercive field compared to the zero field product and the AF matt part, see Table 4.7. The magnitude of this coercive field reduction is 20-30 % for those products synthesised in a flow of oxygen. The annealed AF perchlorate products were also found to have a reduced coercive field compared to the ZF products, although the magnitude of the reduction was less, 4-7 % (~100 Oe compared to ~400 Oe for the non-perchlorate products). In addition, the coercive field values of all of the perchlorate products were lower than the non-perchlorate ones.

In Chapter 3, the reduction in coercive field of the annealed products is attributed to better combustion which leads to fewer pinning centres in the post-SHS / annealed product. Pinning centres are generally defects in the crystalline structure, or at grain boundaries. Fewer pinning centres means less resistance to domain wall motion, and consequently a lower coercivity. ^ 30,41,99

Figure 4.12 is a plot of the maximum magnetisation vs. coercive field for annealed products, grouped according to their synthesis conditions. It is interesting to compare this with the plot of the $a$ and $c$ lattice parameters for the same products, in the same groupings, Figure 4.9. This suggests that the synthesis conditions affect the unit cell volume and the magnetic parameters of the products, although it is not clear quite how the two are related.
Figure 4.12 indicates the possibility that the magnetic parameters of BaFe$_{12}$O$_{19}$ could be tuned by appropriate synthesis conditions. Such a result has potential commercial interest: it means that magnetic field synthesis is a possible alternative to the chemical doping of BaFe$_{12}$O$_{19}$ to reduce its coercivity.

4.4.7 Pre-aligned reactions

The aim of performing pre-aligned reactions was to study a reaction in which the green mixture was reorganised due to a magnetic field, but was not conducted in the magnetic field. This was to answer the question of whether the magnetic field has an effect during the reaction, or whether its influence is restricted to prior reorganisation of the material.

The products from the pre-aligned reactions were similar to those from the 1.1 T reactions; they contained matt and shiny parts, and the shiny part had a reduced coercive field. This suggests that reorganisation of the starting materials is one of the ways that a magnetic field influences the reaction. However, the pre-aligned (non-perchlorate) products did not exhibit a needle-like microstructure and the reaction temperatures reached were not as high as those in the field, suggesting that application of the field during the reaction itself has some additional influence beyond prior reorganisation of the green mixture. This additional influence of the field during the reaction might be its action on ions in liquid phases at the reaction zone, or its action on paramagnetic oxygen.

It should be noted that other researchers in the UCL group had in some cases observed needle-like particles in the pre-aligned shiny products. This was suspected to be due to a higher flow rate of oxygen used in those cases. Indeed, such results prompted us to use a flowmeter to control the amount of oxygen, to reduce the variability between the way the reactions were conducted.

4.4.8 Use of internal oxidising agent, sodium perchlorate

The aim of performing reactions on pressed bars containing sodium perchlorate was to investigate the exclusive effects of the magnetic field by eliminating differences of green mixture shape, density and oxygen diffusivity between zero
field and applied field arrangements. Reactions were also performed on perchlorate-containing powders to compare with the perchlorate bar and the non-perchlorate powder results.

The main findings when using perchlorate were that the differences (temperature, microstructure, coercive field, reaction completeness) between the zero field and applied field products were reduced or eliminated, and the perchlorate products were more completely reacted than their non-perchlorate counterparts.

The zero field, applied field and pre-aligned perchlorate reactions all had the same reaction temperature, and had the same degree of reactant conversion. This contrasts with the non-perchlorate reactions, where the applied field was seen to enhance both the reaction temperature and degree of conversion compared to zero field. All of the perchlorate products exhibited a needle-like microstructure; in the non-perchlorate reactions this was only observed for the applied field products. The annealed perchlorate applied field products exhibited a reduced coercive field compared to the zero field products, the same as for the non-perchlorate case. However, the magnitude of the coercive field reduction is less, ~5 % for perchlorate compared to ~20 % for non-perchlorate products.

The phase composition of the post-SHS products and the magnetic parameters of the annealed products showed that the perchlorate products were more fully combusted than their non-perchlorate counterparts, see Table 4.3 and Figure 4.10. The degree of conversion is related to the reaction temperature. The reactions with perchlorate had the highest observed temperatures (of 1150-1250 °C) and the post-SHS products contained none of the starting materials Fe and Fe₂O₃. The reactions without perchlorate had lower temperatures (ca. 1000 °C) and the post-SHS products contained significant amounts of Fe and Fe₂O₃. This greater degree of conversion in the perchlorate products is explained by the fact that the oxygen source is internal. Oxygen accessibility is therefore a crucial factor in SHS reactions. All of the annealed perchlorate products had lower coercive fields than those without perchlorate, see Table 4.7, which indicates a greater degree of
combustion in the perchlorate reactions. So, an internal oxidising agent leads to
the same kind of effects as a magnetic field, as shown in Figure 4.31.

![Figure 4.31 - Flow diagram of effects due to a magnetic field and use of an
internal oxidising agent (sodium perchlorate).]

4.4.9 Electrical resistivity

The shiny parts of the products from AF and pre-aligned barium ferrite reactions
were silver coloured and looked like they might be metallic. To test the metallic
nature of a shiny part, its electrical resistivity was measured as a function of
temperature – it was found to behave as a semiconductor. A transition was
observed at ~120 K, identified as the Verwey transition of magnetite, Fe$_3$O$_4$. The
Verwey transition is a first order crystallographic transition from cubic spinel to
orthorhombic (or a structure of even lower symmetry). Above the Verwey
transition temperature, magnetite behaves like a poor metal, but below the
transition temperature it distorts to a semiconducting phase and the electrical
conductivity decreases by a factor of 100.\(^{95,100}\) The plot of $\ln$ (resistivity) vs. $1/T$
for the shiny sample (Figure 4.22) resembles the literature plot for Fe$_3$O$_4$.\(^{95}\) The
band gaps calculated for the shiny sample were 76 meV below the Verwey
transition temperature and 66 meV above it; these are comparable with values
reported in the literature of 70-90 meV below the Verwey temperature and 20-
40 meV above it.\(^{100}\)
The post-SHS barium ferrite AF shiny sample is multiphasic, containing in order of abundance \( \text{Fe}_3\text{O}_4 \), \( \text{BaFe}_2\text{O}_4 \), \( \text{Fe}_{1-x}\text{O} \), \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe} \), determined by XRD and Mössbauer analysis. The electric current will travel along the path of least resistance, which will depend not only on the resistivity of each phase present, but also on the distribution of the phases. A percolation effect operates – for example, regions of metallic iron may be present, but if the regions are further apart than the percolation limit, they will not form a path for electrical conduction. Magnetite, \( \text{Fe}_3\text{O}_4 \), is the predominant phase in the shiny part, so it is not surprising that it dominates the electrical conductivity behaviour of the shiny sample. So, the shiny samples are not metallic in nature, but are semiconducting with a small band gap of \( \sim 70 \) meV.

4.4.10 Temperature measurements at high magnetic fields

For the experiments at high magnetic fields, the reaction temperatures were measured by observing the light emitted by reacting pellets, and assuming that they behaved as blackbody radiators.

A hot body gives off a glow, or thermal radiation, emitted from the body’s surface over a range of wavelengths. The spectral emittance (energy flux) of the thermal radiation has a maximum at a certain wavelength; the position of the maximum emittance depends on the temperature of the hot body. For most hot bodies only a fraction of the thermal radiation flux is emitted because the surface is not a perfect emitter. A blackbody however is a perfect emitter and absorber, so its spectral emittance only depends on its temperature. The relationship between the wavelength of maximum spectral emittance, \( \lambda_{\text{max}} \) (in m), and the temperature, \( T \) (in K), of a blackbody is given by Wien’s Law (Eqn. 4.7),

\[
\lambda_{\text{max}} = \frac{hc}{4.9651kT} = \frac{2.898 \times 10^{-3}}{T} \\
\text{Eqn. 4.7}
\]

where \( h \) is Planck’s constant in J s, \( c \) is the speed of light in m s\(^{-1}\), \( k \) is Boltzmann’s constant in J K\(^{-1}\) and 4.9651 is a dimensionless number.
The maximum temperature measured by the spectrometer for all of the reactions was \(-3050\text{ to }3100\,^\circ\text{C}\), which is about double the value of the temperatures measured by optical pyrometry and thermal imaging camera in the lab at UCL. Why might this be? The spectrometer was calibrated against some lamps of known temperature and found to be operating correctly. Smoke was produced during the reaction which would have scattered the light from the reaction, possibly resulting in a higher temperature being recorded than was actually generated by the reaction. Another possibility is that the oxygen flow was different in the set-up at Nijmegen. Flow rates of 18 or \(35\,\text{l/min}^{-1}\) were used at Nijmegen. These were greater than those used in the lab at UCL, of \(\sim 2\,\text{l/min}^{-1}\), where temperatures of \(-1200\,^\circ\text{C}\) were measured in a field of \(1.1\,\text{T}\). In addition, in the UCL lab arrangement some oxygen could potentially escape out of the end of the pipe by back flow, thus reducing the flow rate. Perhaps the most important reason for the higher temperatures recorded at Nijmegen compared to in the lab at UCL, is the fact that the ratio of \(\text{Fe:Fe}_2\text{O}_3\) was different in the two situations. The barium ferrite green mixtures for the pellet reactions at Nijmegen contained a higher ratio of iron fuel to iron oxide limiter than those performed at UCL (in order to get the pellets to ignite), which would significantly increase the temperature reached in those reactions. Therefore it is not fair to compare between the reaction temperatures measured at Nijmegen and at UCL.

The adiabatic combustion temperature for the SHS reaction to form \(\text{BaTiO}_3\) is given in the literature as \(3200\,^\circ\text{C}\). This was determined for a slightly different ratio of \(0.4\,\text{Ti to }0.6\,\text{TiO}_2\) compared to the ratios used in our experiment, but it suggests that the temperatures estimated from the spectrometer results may not be far off the true internal reaction temperatures.

It is possible to calculate the adiabatic combustion temperatures from a knowledge of the specific heat capacity, \(C_p\), and the enthalpy of reaction of the product, \(\Delta H_{r,298\text{K}}\), as described in Chapter 1, Section 1.2.2 (Eqn. 1.3). However, the temperature could not be calculated for \(\text{BaFe}_{12}\text{O}_{19}\), because no data is available for \(C_p\) and \(\Delta H_{r,298\text{K}}\).
Difficulties with using the spectrometer to measure the temperature of SHS reactions include the fact that it collects light (via the optical fibre) from all of the pellet, so this includes reacted, reacting and unreacted parts. An absolute temperature cannot be given because the Ti ignition peak overlaps with the reaction peak. The colour of the pellet may also be an issue, since it will absorb radiation of different frequencies depending on its colour, which would affect the temperature observed.

4.4.11 Influence of a magnetic field on strongly and weakly magnetic systems / Possible mechanisms for the influence of a magnetic field

Some suggested hypotheses for the cause of magnetic field effects were tested. One hypothesis was that the alignment of magnetic materials in the field leads to better mixing of the reactants (better reaction pathways) and hence higher reaction temperatures and more complete combustion. Another hypothesis was that the magnetic field acts on ions at the SHS propagation wavefront. A third hypothesis was that the field acts on paramagnetic oxygen, thereby promoting combustion. These are selected ideas that came to the fore during the course of this investigation (although other explanations for the influence of a magnetic field may exist).

The strategy behind the Nijmegen experiments was as follows:

Hypothesis 1 – reactions are hotter and more complete in a magnetic field because the reactants reorganise in the magnetic field. In this case the reaction temperature should stay about the same for reactions on powders of weakly magnetic reactants, but increase for the strongly magnetic reactants, going from zero field to applied field. (However, in the set-up used at Nijmegen, the temperatures of reactions on powders could not be measured.)

Another way to test the reorganisation hypothesis was to compare the reaction completeness from reactions on powders and pellets for a strongly magnetic system. In this case the reaction completeness should stay about the same for the pellet reactions, but increase for the powder reactions, going from zero field to
The situation is slightly complicated by the fact that the reactions on pellets required a different flow rate to the reactions on powders. So a difference in the reaction completeness might be seen if the field operates by acting on oxygen (Hypothesis 3), rather than due to reorganisation.

Hypothesis 2 – reactions are hotter and more complete in a magnetic field because the field acts on ions at the SHS propagation wavefront. In this case the temperature should increase for both the strongly magnetic and weakly magnetic reactants going from zero to applied field, because the wavefront will generate ions regardless of whether the system is strongly or weakly magnetic.

Hypothesis 3 – reactions are hotter and more complete in a magnetic field because the field acts on paramagnetic oxygen, thereby promoting combustion. This idea could not be distinguished from the idea described in Hypothesis 2, because all of the systems tested here involved oxygen.

The raw spectrometer data for BaFe_{12}O_{19}, Figure 4.27, shows a qualitative difference between the spectra collected in zero field compared to in magnetic fields of 5 to 20 T. This difference is not so certain in the data for BaTiO_3, Figure 4.28, since only two data sets are available for comparison.

The spectrometer data shown in Figure 4.29 suggests that the magnetic field may have an effect on both the strongly magnetic BaFe_{12}O_{19} system and the weakly magnetic BaTiO_3 system. For both BaFe_{12}O_{19} and BaTiO_3 the wavelength of the reaction peak increases more quickly as the magnetic field strength increases, see Figure 4.29 (a) and (c), and this corresponds to more rapid cooling. The plots also finish after a shorter time in the magnetic field compared to zero field, which means that a peak could no longer be identified for the reaction, again pointing to more rapid cooling.

The intensity of the reaction peak depends on the amount of light emitted by the reaction wavefront. As the pellet cools after the wavefront has passed, less light is
emitted and the wavelength of the emitted light increases. The plots of intensity vs. time can thus be related to cooling of the reacted pellets. For the BaTiO₃ reaction, Figure 4.29 (d), the intensity decreases more rapidly in the 5 T reaction compared to in zero field. A similar effect can be seen in the BaFe₁₂O₁₉ results in 20 T compared to zero field, Figure 4.29 (c). The intensity of the 5 T and 15 T reactions increases after the initial peak – this may be due to the reaction not proceeding smoothly across the pellet, or perhaps pellet movement might temporarily obscure the light from the reaction.

In summary of the spectrometer data, a magnetic field of 5-20 T appears to have an effect on both strongly and weakly magnetic systems. This is evidence to support the hypotheses that the magnetic field acts on ions at the SHS wavefront, and/or that the field acts on paramagnetic oxygen, promoting combustion. Further evidence is required to establish whether the field really does affect weakly magnetic as well as strongly magnetic systems, given previously published results stating that a magnetic field does not affect non-ferromagnetic systems.⁵⁵

Another point to consider is the direction of the magnetic field relative to the direction of SHS propagation in the pellet. In pellets, the propagation wave proceeds along the diameter of the pellet. Figure 4.6 shows the orientation of the pellet as it is loaded into the magnet. If the pellet stayed in this orientation when the field is switched on, the wave direction would be perpendicular to the magnetic field direction. There is a precedent in the literature for a transverse field to affect reactions on pellets containing a ferromagnetic component⁵⁹ – a change in structure and composition of the product was observed, but no change in reaction velocity. However, the pellet does not stay in the orientation in which it was loaded. Instead it flips up so that its diameter is parallel with the magnetic field (it has room to do this). The direction of the wave is therefore parallel to the magnetic field direction, since the pellet is ignited from the top and the propagation wave should travel downwards along the magnetic field. Experiments have not been reported in the literature for a propagation wave travelling parallel
to a magnetic field direction, for pellets, although a parallel field has been reported to influence SHS reactions on powders.

The reaction completeness of the weakly magnetic SrTiO$_3$ and the strongly magnetic BaFe$_{12}$O$_{19}$ systems was determined by XRD of the post-SHS products. The SrTiO$_3$ reactions essentially went to completion at all magnetic field strengths, for both pellets and powders. It was therefore not possible to tell by this route if a magnetic field affects weakly magnetic systems. For the strongly magnetic system, BaFe$_{12}$O$_{19}$, the reaction did not go to completion at any field strength, for both pellets and powders. The XRD results (Table 4.8) did not show any trends in reaction completeness.

The VSM results (Table 4.9) suggest that the magnetic field may influence reactions on powders differently to reactions on pellets. The maximum and remanent magnetisation values for the barium ferrite post-SHS powder products were found to decrease with increasing magnetic field strength. No such trend was observed for the reactions on pellets.

4.5 Conclusions

An applied magnetic field of 1.1 T has an effect on barium ferrite powder reactions ignited under a flow of oxygen. It leads to hotter and faster reactions, a greater degree of conversion of the reactants in the SHS step, an altered fibrous macrostructure, an altered needle-like microstructure, and a reduced coercive field of the annealed product. The magnetic field may also affect the combustion itself and the way the reaction goes; this aspect is discussed in Chapter 5 on time-resolved X-ray diffraction.

Using sodium perchlorate as an internal source of oxygen gives similar effects as a magnetic field, whether the reactions are performed in or out of a field, and on powders or pellets. So, the unique effects of the field are a fibrous macrostructure and possibly a different reaction route. The magnetisation and coercive field of barium ferrite are modified by synthesis in a magnetic field and by using an internal oxidising agent such as sodium perchlorate. This has potential
commercial value as an alternative to chemical doping as a means of controlling coercive field.

There is a wide variety of experiments that could be performed in relation to the influence of magnetic fields on SHS. In the experiments described in this chapter a constant magnetic field was applied during the reaction, supplied either by a permanent magnet (1.1 T) or by an electromagnet (up to 20 T). However, an electromagnet could be used to change the field strength as the reaction progresses. It might be possible by this route to produce solid bodies of magnetic material with variable magnitude and direction of magnetisation along their length. Magnetic and electric fields are closely linked: electromagnetic radiation consists of oscillating electric and magnetic fields. It could be interesting to perform SHS reactions in a microwave, to see if microwave radiation influences the reactions.

Three hypotheses have been proposed to explain why the magnetic field has an effect on these SHS reactions and products. Reorganisation of the green mixture in the magnetic field, leading to better reaction pathways, is one hypothesis. Experiments described in this chapter have provided evidence for reorganisation as being one way that the field acts; in particular, effects being observed for pre-aligned reactions, and a magnetic field affecting the magnetisation of post-SHS products from reactions on powders but not pellets. Experiments performed at high magnetic fields suggest that a magnetic field may affect reactions on both strongly and weakly magnetic systems. Reactions in magnetic fields of 5-20 T appeared to cool more quickly than in zero field for both the ferrimagnetic BaFe_{12}O_{19} and the paramagnetic BaTiO_{3} systems. There is therefore some evidence to support the other suggested hypotheses, namely the field acting on ions at the SHS wavefront, and the field acting on paramagnetic oxygen. Future experiments on carefully chosen systems (for example, those not requiring oxygen) in a range of magnetic fields should provide further valuable information on why a magnetic field affects SHS reactions.
5 Time-resolved X-ray diffraction studies

5.1 Introduction

Time-resolved X-ray diffraction (TRXRD) is a technique which has been used to study reactions in situ. In this chapter the first TRXRD studies of SHS reactions to form ferrites are described. The aim was to aid our understanding of these SHS reactions by gaining information on the reaction pathways and any intermediates that may have been formed, transformation times from reactants to products (reaction timescales), and thermal relaxation of the product after the passage of the SHS wave. The previous chapters have shown that processing parameters and magnetic fields influence the reaction (temperature and velocity) and the products (microstructure, degree of combustion, magnetic properties). It was hoped that TRXRD would help provide a better understanding of these influences.

Because these were the first TRXRD studies of SHS reactions to form ferrites, and the first in magnetic fields, much of the work presented here is the outcome of a necessary learning experience. It was important to establish the best way to perform the reactions in order to get repeatable results. These were also the first TRXRD studies of SHS reactions to use energy-sensitive, rather than position-sensitive, detectors.

TRXRD has been used for the last 20 years to investigate a variety of reactions in situ. Examples of the use of TRXRD include studies of hydration and crystallisation processes. The frequency of recording diffraction patterns in these examples is typically of the order of minutes or hours between scans. TRXRD has also been used to study SHS reactions, but here the frequency of recording is much faster, ~10-100 ms between scans, due to the fast nature of SHS. The first reported TRXRD study of SHS was in 1981, for the Ni-Al system.

A requirement of TRXRD is the fast collection of diffraction patterns. This is achieved by using high intensity X-rays from a synchrotron radiation source, and
an experiment set-up that allows the fast readout of diffraction patterns over a range of 2θ diffraction angles, for example, a bank of detectors. The improvements in the quality of TRXRD data over the last 20 years have been summarised by Gras and Charlot.\textsuperscript{87,91}

The bulk of the work in the literature on TRXRD of SHS has been on intermetallic systems. Experiments have been performed at various synchrotron sources, for example, ESRF and LURE (France), and Brookhaven (USA). The main subjects of study have been binary or ternary intermetallic/elemental systems such as Ti-Si\textsuperscript{88}, Ta-C\textsuperscript{86}, Fe-Al\textsuperscript{87,104}, Mo-Si\textsuperscript{91} and Al-Ni-Ti\textsuperscript{105}. Compacted pellets of green mixture were used and ignited by resistive heating (tungsten coil). Reactions were performed either in a helium atmosphere or under vacuum to avoid oxidation, which necessitated the use of a contained reaction chamber. Monochromatic X-rays were used; the wavelength varied from experiment to experiment, and was chosen where possible to suit the materials under investigation. Position-sensitive detectors were used, with varying 2θ ranges, and were centred at those angles where the diffraction maxima were expected. Typical ranges covered by the detectors mentioned in the literature vary from 6° up to 38° 2θ. The best time resolution reported is 50 ms.\textsuperscript{91} Time resolution is the time between each diffraction pattern – it is equal to the exposure time for each pattern plus the time taken for the detector to readout the data for each pattern. Some papers quote a lower time resolution of 30 ms, but either no mention is given of the readout time,\textsuperscript{105} or several scans had to be summed to overcome signal/noise problems.\textsuperscript{104}

Some examples from the literature demonstrate the usefulness of the TRXRD technique. Reactions on the Ta-C system were performed to investigate the reaction mechanisms of purely solid state (homogeneous combustion) SHS.\textsuperscript{86} TRXRD data taken at 100 ms and 50 ms / scan showed that the reaction to form TaC proceeded via a Ta$_2$C intermediate phase, whereas the reaction to form Ta$_2$C did not pass through any intermediate steps. From the time-resolved data, plots of the relative concentration of each phase vs. time were drawn, which enabled the
time for TaC formation to be estimated at 3-4 s. Another example is a study of the reaction between Mo and Si to form MoSi$_2$. The authors wanted to investigate whether mechanical activation of the starting materials would modify the reaction pathway. No intermediates were observed, even at such short time resolutions of 50 ms / scan, and no new phases appeared after the wave had passed. The TRXRD data was plotted as volumetric fraction vs. time, which showed that the decomposition of the reactants and the formation of the product happened simultaneously.

Not all the published work on time-resolved XRD has been performed on synchrotron sources. Kachelmyer et al. reported TRXRD results obtained on a lab-based X-ray diffractometer, with a 2 kW copper anode X-ray tube. A 1D position-sensitive detector with 1024 pixels was used, having a $38^\circ$ 2$\theta$ angular range ($24^\circ$-62$^\circ$). The reaction to form Ti$_5$Si$_3$ was investigated. The time resolution was 1 s, although the authors claimed a resolution down to 100 ms was possible.

The details of the TRXRD experiments performed for this thesis are given in Chapter 2. The experiments performed at the ESRF were similar in set-up to those described in the literature, i.e. monochromatic X-rays and a position-sensitive detector covering a range of 2$\theta$. The Daresbury experiments however were unique, because instead of a monochromatic beam of X-rays, a white beam was used, and instead of a bank of position-sensitive detectors over a range of 2$\theta$, three fixed energy-sensitive detectors were used. This energy-dispersive set-up has been used for other TRXRD experiments (see for example Colston et al., Fogg et al.), but for much longer collection times, and never for SHS reactions. The Daresbury and ESRF experiments were also unique because they were, to our knowledge, the first TRXRD studies of oxides, in air, and the first such studies of reactions in magnetic fields.

Alternative ways to study reactions in situ include digital high speed microscopic video recording and quenching (quasi-in situ). These techniques are discussed in Chapter 3, Section 3.1.4.
5.2 Experimental

The experimental details are described in Chapter 2. A summary of the different experiments performed is given in Table 5.1. Reactions were performed on barium ferrite and Fe/Fe$_2$O$_3$ green mixtures, in pellet and powder forms, in zero field (ZF) and applied magnetic fields (AF) of 0.2 T and 1.1 T. Barium ferrite was chosen because it had been studied in magnetic fields, and Fe/Fe$_2$O$_3$ was chosen to complement the barium ferrite reactions.

Table 5.1 – Time-resolved X-ray diffraction experiments performed.

<table>
<thead>
<tr>
<th>Experiment location</th>
<th>Daresbury</th>
<th>ESRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of experiment</td>
<td>July 99</td>
<td>Sept 00</td>
</tr>
<tr>
<td>Detector readout time / s</td>
<td>~2</td>
<td>0.75</td>
</tr>
<tr>
<td>Beam spot (pinhole) size / mm</td>
<td>0.5, 1</td>
<td>0.5</td>
</tr>
<tr>
<td>BaFe$<em>{12}$O$</em>{19}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZF</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>0.2 T</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>1.1 T</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Fe/Fe$_2$O$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZF</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>0.2 T</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>1.1 T</td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

The July 99 and September 00 Daresbury experiments were on powders, while the February 01 experiments were performed exclusively on pellets. The ESRF experiments included a few reactions on pellets. Pellets were used for several reasons: to avoid separation of the green mixture in the magnetic field, to stop the components moving in the field during the reaction, to give a well-defined wave direction vs. beam direction, to allow mass consistency between runs, and to eliminate as many differences as possible between the zero and applied field set-ups.

Table 5.2 shows how the measured range for the Daresbury and ESRF experiments corresponds to a 2θ range for the copper anode wavelength of
1.54 Å. At Daresbury the measured range depended on the angle of the detector, whereas at the ESRF it depended on the sample to detector distance.

Table 5.2 – Equivalent 2θ ranges for the detectors at Daresbury and ESRF.

<table>
<thead>
<tr>
<th>Detector</th>
<th>X-ray wavelength</th>
<th>Measured range</th>
<th>Equivalent 2θ range for Cu λ of 1.54 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daresbury 16.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>White beam</td>
<td>5-112 keV</td>
<td>5°-131 °</td>
</tr>
<tr>
<td>Middle</td>
<td></td>
<td></td>
<td>3°-69°</td>
</tr>
<tr>
<td>Bottom</td>
<td></td>
<td></td>
<td>1°-25°</td>
</tr>
<tr>
<td>ESRF ID-11</td>
<td>CCD camera</td>
<td>0.2952 Å</td>
<td>0.5°-12° (2θ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3°-66°</td>
</tr>
</tbody>
</table>

A comparison of the specifications for the experiments at Daresbury and ESRF is given in Table 5.3. This shows that at Daresbury a smaller minimum d-spacing could be measured. However, the ESRF had a significantly better time resolution, due to the shorter readout time of the detector. This meant that the ESRF was better for collecting high time resolution data for the reactions, whereas Daresbury was better suited to longer scans, and experiments with single scans, i.e. moving the beam spot relative to the sample to check for homogeneity.

Table 5.3 – Comparison of the experiment specifications between Daresbury and ESRF.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Daresbury 16.4</th>
<th>ESRF ID-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray wavelength</td>
<td>White beam</td>
<td>0.2952 Å</td>
</tr>
<tr>
<td>Beam spot diameter</td>
<td>0.5-2.0 mm</td>
<td>0.2 mm</td>
</tr>
<tr>
<td>Minimum d-spacing</td>
<td>~0.8 Å</td>
<td>~1.4 Å</td>
</tr>
<tr>
<td>Detector readout time</td>
<td>250 ms - 2 s</td>
<td>80 ms</td>
</tr>
<tr>
<td>Minimum exposure time</td>
<td>100 ms</td>
<td>50 ms</td>
</tr>
<tr>
<td>Best scan rate</td>
<td>3 scans / s</td>
<td>8 scans / s</td>
</tr>
</tbody>
</table>

The time resolution of 130 ms (50 ms exposure time and 80 ms readout, at the ESRF) is not as good as the best reported times of 50 ms. However, for those fastest reported times, the data collection was over a narrower range of 2θ (30°),
of a lower resolution (256 channels) and of strongly scattering intermetallic samples.

5.2.1 TRXRD at Daresbury Station 16.4

The program DL Converter\textsuperscript{106} was used to convert the raw data from channels to energy, by using the information in Table 5.4 with Eqn. 5.1,

\[ E = (B \times \text{channel number}) + A \]

Eqn. 5.1

where \( E \) = energy corresponding to the data recorded in a particular channel of the detector, \( A \) = initial (start) energy, \( B \) = step in the energy, all in units of keV. The \( A \) and \( B \) values were determined by experiment and depended on the particular detector in question.

Table 5.4 – Daresbury detector details, required for data processing.

<table>
<thead>
<tr>
<th>Date of experiment</th>
<th>Detector</th>
<th>( A ) (start) / keV</th>
<th>( B ) (step) / keV</th>
<th>( 2\theta ) / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 99</td>
<td>Top</td>
<td>5.9439</td>
<td>0.02664</td>
<td>7.47</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>5.8247</td>
<td>0.02680</td>
<td>4.67</td>
</tr>
<tr>
<td>Sept 00</td>
<td>Top</td>
<td>4.38</td>
<td>0.02966</td>
<td>7.86</td>
</tr>
<tr>
<td>Feb 01</td>
<td>Top</td>
<td>4.4094</td>
<td>0.02964</td>
<td>6.95</td>
</tr>
</tbody>
</table>

To convert energy to d-spacing, Bragg’s Law (Eqn. 5.2) and Eqn. 5.3 were used:

\[ \lambda = 2d \sin \theta \]

Eqn. 5.2

\[ E = h\nu = \frac{hc}{\lambda} \]

Eqn. 5.3

Substituting Eqn. 5.2 into Eqn. 5.3 gives Eqn. 5.4,

\[ E = \frac{hc}{2d \sin \theta} \]

Eqn. 5.4
where \( E = \) energy in keV, \( h = \) Planck's constant expressed in keV s, \( c = \) speed of light expressed in Å s\(^{-1}\), \( d = \) d-spacing of the sample in Å, and \( \theta = \) angle of the detector in degrees. Rearranging \( d \) and \( E \), substituting the values for the constants \( h \) and \( c \), and recognising that if the angle of the detector is expressed in 2\( \theta \) then \( \theta = \frac{2 \theta_{\text{detector}}}{2} \), gives Eqn. 5.5,

\[
d = \frac{6.199}{E \sin(2 \theta_{\text{detector}}/2)} \tag{Eqn. 5.5}
\]

where \( d \) is in Å, \( E \) is in keV and \( 2 \theta_{\text{detector}} \) is in degrees. Eqn. 5.5 was used to convert the x-axis scale of the diffraction patterns from energy to d-spacing. The patterns could be further converted into an equivalent 2\( \theta \) scale, say for a copper anode, by substituting \( \lambda = 1.54 \) Å and the data in d-spacings into Bragg's Law (Eqn. 5.2), where \( \theta = \frac{2 \theta}{2} \). The converted data was then viewed with the program Xfit\(^{107}\). Plots in 2D and 3D were created using the programs ASAD\(^{108}\) (to convert 8 column data to 1 column), PGPlot\(^{109}\) and UNIMAP,\(^{110}\) available through Daresbury.

The angles of the detectors given in Table 5.4 were calculated from a silicon powder calibration. The channel number of the (111) peak of silicon was identified and substituted into Eqn. 5.1, then the corresponding energy was substituted into Eqn. 5.5, to give the detector angle in 2\( \theta \).

Each detector has 4000 channels. The response is not linear across all 4000 channels. The best response of each detector is over the middle 2000 channels, which corresponds to 34-82 keV for all 3 detectors. In terms of d-spacings, the region of best response is given in Table 5.5. This is something that must be taken into consideration when interpreting the results from the top detector compared to the middle detector. The bottom detector was not used because its region of best response fell outside the range of d-spacings for the samples used in this work. For the barium ferrite reactions, the peaks for the starting materials and products
have d-spacings from 1.17 Å to 3.64 Å, with most of the peaks in the range 1.70 Å to 3.64 Å.

Table 5.5 – Region of best response for each detector at Daresbury Station 16.4.

<table>
<thead>
<tr>
<th>Detector</th>
<th>Region of best response, d-spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>2.97 Å to 1.13 Å</td>
</tr>
<tr>
<td>Middle</td>
<td>4.75 Å to 1.81 Å</td>
</tr>
<tr>
<td>Bottom</td>
<td>12.2 Å to 4.65 Å</td>
</tr>
</tbody>
</table>

The detector resolution, in terms of the step size per channel, was 66°/4000 channels (for the middle detector), which equals 0.0165° / channel.

When comparing results from the top detector with those from the middle detector, a particular Bragg peak will appear at a different energy in each detector. This can be seen by considering Eqn. 5.5. For example, if \( d = 2.53 \) Å, \( E = 38 \) keV in the top detector, but \( 60 \) keV in the middle detector.

The results from the TRXRD experiments at Daresbury could be output in a number of formats, including stack plots of individual diffraction patterns, 2D plots showing each pattern as a series of coloured/light or dark spots, and 3D contour plots of energy, scan number (time) and intensity.

5.2.2 TRXRD at ESRF Beamline ID-11

A "caking" program (mi517cake.sh for SHS runs, korcake.sh for single scans)\(^{111}\) was performed on each series of results which were recorded as diffraction ring patterns by the CCD camera detector. This program subtracted the dark current and readout noise, corrected the data for spatial distortion due to the curvature of the detector, then integrated around the ring to give a powder diffraction pattern of intensity vs. 2\( \theta \).
The detector resolution, in terms of the step size per channel, was 63°/512 channels, which equals 0.123° / channel.

The results from the TRXRD experiments at the ESRF could be output in a number of formats. Pictures of the diffraction rings could be recorded, which gave useful information. Three-dimensional plots of 2θ (for λ = 0.2952 Å), scan number (time) and intensity were produced, showing every 5th scan for clarity. Close-ups of the reaction regions in 3D showed every scan. The time between each recorded scan was 130 ms (50 ms exposure + 80 ms readout), so the time between every 5th scan is 650 ms.

5.3 Results

5.3.1 Fe/Fe$_2$O$_3$

The TRXRD results from a zero field reaction of Fe + Fe$_2$O$_3$ + O$_2$ are shown in Figure 5.1. In Figure 5.1 some peaks can be seen to come in then go away. These intermediate peaks, at about 8 and 11° 2θ, correspond to wüstite, Fe$_{1-x}$O. In the reference pattern$^{112}$, the (2 0 0) peak is at 7.86°, $d = 2.153$ Å; and the (2 2 0) peak is at 11.12°, $d = 1.523$ Å. Two zero field runs were recorded, where the Fe$_{1-x}$O peaks persisted for either 50 or 90 scans, corresponding to either 6 or 12 s. A little Fe$_{1-x}$O remains in the product, along with Fe$_2$O$_3$ and Fe$_3$O$_4$. After the reaction the peak positions did not appear to shift, i.e. no thermal relaxation was observed.

The TRXRD results from a reaction of Fe + Fe$_2$O$_3$ + O$_2$ in an applied field of 0.2 T are shown in Figure 5.2. In Figure 5.2 the diffraction patterns have peak intensities which vary erratically with time. No intermediate phases are observed in the ESRF results. The products contain Fe$_3$O$_4$, Fe$_2$O$_3$ and a little Fe$_{1-x}$O. After the reaction the peak positions did not appear to shift, i.e. no thermal relaxation was observed.
Selected results from the experiments at Daresbury for the Fe/Fe$_2$O$_3$ reactions are shown in Figure 5.3.

Figure 5.1 – Fe/Fe$_2$O$_3$ zero field powder reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown).

Figure 5.2 – Fe/Fe$_2$O$_3$ 0.2 T powder reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown).
Figure 5.3 – Daresbury data (scan number vs. energy) for Fe/Fe₂O₃ powder reactions: (a), (b) zero field; (c) 0.2 T; (d) 1.1 T.

Some diffraction ring patterns recorded during the Fe/Fe₂O₃ reactions are shown in Figure 5.4. The pattern of the green mixture is a series of sharp rings, Figure 5.4 (a). The patterns taken like snapshots during the zero field and the 0.2 T reactions both show spots appearing in some of the diffraction rings during the reactions, Figure 5.4 (b-e).
Figure 5.4 – Diffraction ring patterns recorded at ESRF, for Fe/Fe$_2$O$_3$ reactions of powders. (a) Green mixture pattern, recorded in 0.2 T field, (b)-(e) patterns recorded *in situ* during the reactions: (b) zero field, (c) 0.2 T field, (d) close-up view of the zero field pattern, (e) close-up view of the 0.2 T pattern. Spots appear in some of the rings during the reaction.
The post-SHS products from the zero field and 0.2 T reactions were analysed by recording a single diffraction pattern of each product for a longer time, ca. 10 s. These single scan patterns are shown in Figure 5.5. The zero field products gave patterns almost the same as each other, indicating good reproducibility between runs. The diffraction patterns for the 0.2 T products are in reasonable agreement, although there is some variation between the relative peak heights between runs. Comparing between the zero field and applied field patterns, it can be seen that the phase composition of the post-SHS products varies from zero field to applied field.

Figure 5.5 – Single scan diffraction patterns of the post-SHS products from Fe/Fe$_2$O$_3$ reactions of powders in (a) zero field and (b) 0.2 T, recorded at ESRF.
5.3.2 \textit{BaFe}_{12}O_{19}

The TRXRD results from a zero field reaction of $\text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 + \text{O}_2$ are shown in Figure 5.6. In Figure 5.6, the $\text{BaO}_2$ and Fe peaks disappear, while some $\text{Fe}_2\text{O}_3$ remains, and $\text{Fe}_{1-x}\text{O}$ and $\text{BaFe}_2\text{O}_4$ peaks come in. No intermediate peaks are observed. In some runs the peak positions were observed to shift to higher energies or 2$\theta$ after the reaction.

![Diagram of phase changes](image)

**Figure 5.6** – $\text{BaFe}_{12}O_{19}$ zero field powder reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown). Some of the main peaks for each phase are labelled.

The TRXRD results from a 0.2 T applied field reaction of $\text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 + \text{O}_2$ are shown in Figure 5.7. No intermediates were observed during the reaction. Phases identified in the product included $\text{BaFe}_2\text{O}_4$, $\text{Fe}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3$. The peak positions were observed to shift to higher energies or 2$\theta$ values after the reaction, for some runs, indicating thermal relaxation.
Figure 5.7 – BaFe_{12}O_{19} 0.2 T powder reaction, ESRF data, 50 ms per scan (250 scans total, every 5th scan shown). Note that in this figure the first scan is at the front (opposite orientation to the other figures).

The TRXRD results from a 1.1 T reaction of BaO₂ + Fe + Fe₂O₃ + O₂ are shown in Figure 5.8 and Figure 5.9. Figure 5.8 shows data recorded at Daresbury, whereas Figure 5.9 shows data collected at the ESRF.

Figure 5.8 shows a large intermediate peak at 59-60 keV. It was observed in four out of five repeat runs in 1.1 T. It exists for 4 scans, or ~9 s, and corresponds to the (3 1 1) peak of Fe₃O₄. In the reference pattern for magnetite the (3 1 1) peak has a d-spacing of 2.532 Å which corresponds to an energy of 60.09 keV (for the middle detector). Figure 5.10 is a 2D plot of scan number vs. energy for the same reaction as shown in Figure 5.8. It shows a bright spot in the middle detector corresponding to the large peak. In 3D, Figure 5.11, the large peak is clearly seen. Phases identified in the product included Fe₃O₄, BaFe₂O₄ and Fe₇-xO.

In Figure 5.9 no obvious intermediates are observed. Phases identified in the product included Fe₃O₄ and BaFe₂O₄. The peak positions were seen to shift to higher energies or 20 after the reaction, for some runs, indicating thermal relaxation.
Figure 5.8 – BaFe$_{12}$O$_{19}$ 1.1 T powder reaction, Daresbury July 99 data (middle detector). The numbers on the right hand side are the scan numbers. Each scan was recorded for 250 ms and the time between each scan is 2 s.

Figure 5.9 – BaFe$_{13}$O$_{19}$ 1.1 T pellet reaction, ESRF data, 50 ms per scan (250 scans total, every 5$^{th}$ scan shown).
Figure 5.10 – 2D plots (scan number vs. energy) for BaFe$_{12}$O$_{19}$ 1.1 T powder reaction, Daresbury July 99 data: (a) middle detector, (b) top detector. The brighter colours indicate the more intense peaks.

Figure 5.11 – 3D plots (scan number, energy, intensity) for BaFe$_{12}$O$_{19}$ 1.1 T powder reaction, Daresbury July 99 data: (a) middle detector, (b) top detector.

Selected results from the Daresbury experiments are also shown in Figure 5.12.
Figure 5.12 – Daresbury data (scan number vs. energy) for BaFe$_{12}$O$_{19}$ reactions: (a), (b) zero field (powders); (c), (d) 0.2 T (pellets); (e)-(h) 1.1 T (e, f, g – powders, h – pellet).
The reaction timescale is the time taken for the reactants to transform to the products. An example of how the reaction timescales were estimated is shown in Figure 5.13, for a BaFe$_{12}$O$_{19}$ zero field reaction. The last diffraction pattern that looked like the pattern for the starting materials and the first diffraction pattern that looked like the pattern for the post-SHS product were identified, then the number of scans between them was counted. Knowing the scan time, which equals the exposure + readout time, allowed the reaction timescales to be measured. The timescales for the BaFe$_{12}$O$_{19}$ reactions are given in Table 5.6. These were estimated from the Daresbury and ESRF results, from reactions on powders and pellets. The reaction timescales are difficult to compare because of different volumes sampled by the beam in the different set-ups, and a lack of knowledge of the wavefront direction relative to the beam.

![Diagram](image)

Figure 5.13 – BaFe$_{12}$O$_{19}$ zero field powder reaction, ESRF data, 50 ms per scan (every 2 scans shown). In this reaction region plot, the diffraction patterns for the starting material and the products are shown in red and the number of scans between them is used to estimate the reaction timescale.
Table 5.6 – BaFe$_{12}$O$_{19}$ reaction timescales, estimated from time-resolved X-ray diffraction data.

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Estimated reaction timescales / s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ESRF</td>
</tr>
<tr>
<td>ZF (pellet)</td>
<td>-</td>
</tr>
<tr>
<td>ZF (powder)</td>
<td>3.38</td>
</tr>
<tr>
<td>0.2 T (powder)</td>
<td>3.9</td>
</tr>
<tr>
<td>1.1 T (powder)</td>
<td>3.9</td>
</tr>
</tbody>
</table>

A diffraction ring pattern for a BaFe$_{12}$O$_{19}$ zero field reaction is shown in Figure 5.14. The diffraction patterns for the zero field, 0.2 T and 1.1 T looked similar; they were made up of sharp rings without many spots.

Figure 5.14 – Diffraction ring pattern recorded at ESRF in situ during the zero field powder reaction of BaO$_2$ + Fe + Fe$_2$O$_3$ + O$_2$: (a) complete zero field pattern, (b) close-up of (a). The rings are sharp and do not contain many spots.
Figure 5.15 – Single scan diffraction patterns of the post-SHS products from BaFe$_{12}$O$_{19}$ reactions on pellets and powders in (a) zero field, (b) 0.2 T and (c) 1.1 T, recorded at ESRF.
The post-SHS products from the zero field, 0.2 T and 1.1 T reactions were analysed with single scans and their diffraction patterns are shown in Figure 5.15. The patterns for the zero field products from different runs are in good agreement, whereas for 0.2 T and 1.1 T the patterns do not overlap. This suggests that reproducibility between runs is more difficult to obtain when performing reactions inside a magnetic field.

### 5.4 Analysis and Discussion

#### 5.4.1 Fe/Fe₂O₃

The zero field and applied field reactions of Fe + Fe₂O₃ + O₂ both end with the same phases in the products: Fe₂O₃, Fe₃O₄ and a little Fe₁ₓO. However, the reaction pathways in zero and applied fields were different. In the zero field reaction, wüstite (Fe₁ₓO) was observed as an intermediate phase, whereas no intermediate phase was seen in the applied field reactions. This result suggests that in Fe/Fe₂O₃ reactions the reaction pathway may be influenced by a magnetic field.

![Relative abundance](image)

**Figure 5.16** – Relative abundance of each phase vs. time, for the powder reaction of Fe + Fe₂O₃ + O₂, in zero field, determined by analysis of TRXRD results. Fe₁ₓO, wüstite, is observed as an intermediate phase.
By identifying the phases associated with the various peaks in the zero field reaction of \( \text{Fe} + \text{Fe}_2\text{O}_3 + \text{O}_2 \), from Figure 5.1, a rough plot of the relative abundance of each phase vs. time was obtained, see Figure 5.16. This shows that Fe is used up in the reaction, Fe\(_2\)O\(_3\) is used and then formed, Fe\(_{1+x}\)O is formed and then consumed, and Fe\(_3\)O\(_4\) is formed. A probable reaction pathway is that Fe and Fe\(_2\)O\(_3\) combine, with oxygen, to form Fe\(_{1+x}\)O and Fe\(_3\)O\(_4\). The Fe\(_{1+x}\)O phase is oxidised to form Fe\(_3\)O\(_4\) and Fe\(_2\)O\(_3\), and some Fe\(_3\)O\(_4\) may also form Fe\(_2\)O\(_3\) upon further oxidation. This is summarised in the reaction scheme for Fe/Fe\(_2\)O\(_3\) reactions, Figure 5.17.

\[
\begin{align*}
\text{Fe} + \text{Fe}_2\text{O}_3 & \rightarrow \text{Fe}_{1+x}\text{O} + \text{O}_2 \\
\text{Fe} + \text{Fe}_2\text{O}_3 & \rightarrow \text{Fe}_3\text{O}_4 + \text{O}_2
\end{align*}
\]

**Figure 5.17 – Reaction scheme for the reaction of \( \text{Fe} + \text{Fe}_2\text{O}_3 \) in the presence of oxygen.**

Spots appeared in the diffraction rings during the course of both zero and applied field Fe/Fe\(_2\)O\(_3\) reactions. Spots appear when there are not enough crystallites in the sample to diffract to each part of the ring. This is the case when there are large crystallites and fewer of them, i.e. a coarse powder. Crystallites larger than \( \sim 10 \mu\text{m} \) give rise to spotty diffraction rings.\(^{114}\) Spots can also appear when the crystallites have a degree of preferred orientation, because it is the random orientation of crystallites that is responsible for diffraction to all parts of the ring. The fact that the crystallites are not there in the green mixture, but appear during the reaction, suggests that in the region of the X-ray beam some material melts and recrystallises. Iron melts at 1535 °C, Fe\(_2\)O\(_3\) melts at 1565 °C, Fe\(_3\)O\(_4\) melts at 1594 °C and Fe\(_{1+x}\)O melts at 1369 °C;\(^{93}\) this suggests that internal temperatures reach in excess of 1369 °C. If each diffraction ring was matched with its
corresponding Bragg peak in the diffraction pattern, that would give information on when crystallites appear and which phases they correspond to. The appearance of crystallites should be borne in mind when analysing the data, since the spots may affect the summed intensities around each ring, and therefore the relative peak heights from the different rings.

In the 0.2 T runs, the peak heights varied erratically with time, (Figure 5.2), whereas in zero field the peak heights varied smoothly. The height of a diffraction peak is related to the amount of material present – the number of parallel planes. Variation in the peak height suggests that the amount of material sampled by the X-ray beam changes over a few scans; this could be due to melting and recrystallisation processes, or movement of crystallites in and out of the X-ray beam. The peak height variation cannot just be due to melting and recrystallisation processes, since spotty diffraction rings were seen for both zero and applied field reactions. It is likely that crystallites would move during the reaction, perhaps more so in a magnetic field, and particularly for reactions on powders. Performing reactions on pellets could reduce the movement of crystallites in and out of the beam, which might lead to a smoother variation in the peak heights over time.

5.4.2 \( \text{BaFe}_{12}\text{O}_{19} \)

Barium ferrite is not made in the SHS step, in the reaction of \( \text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 + \text{O}_2 \). Instead, the post-SHS product contains partly reacted phases such as \( \text{Fe}_3\text{O}_4 \), \( \text{Fe}_2\text{O}_3 \), \( \text{BaFe}_2\text{O}_4 \) and \( \text{Fe}_{1-x}\text{O} \). The phases identified in the product depended on whether the synthesis was in zero field, 0.2 T or 1.1 T; for example, \( \text{Fe}_{1-x}\text{O} \) was observed in zero field but not in applied field, whereas \( \text{Fe}_3\text{O}_4 \) was not seen in zero field but was seen in applied field. The proposed reaction scheme for \( \text{BaFe}_{12}\text{O}_{19} \) is given in Chapter 4, Figure 4.30. It shows those phases that have been isolated in the post-SHS products, and the most likely route from the reactants to each of these phases. For example, Fe reacts with oxygen to form \( \text{Fe}_{1-x}\text{O} \), which may then be further oxidised to form \( \text{Fe}_3\text{O}_4 \) or \( \text{Fe}_2\text{O}_3 \), or combine with \( \text{Fe}_2\text{O}_3 \) to form \( \text{Fe}_3\text{O}_4 \).

A large transitory peak was observed in four out of five of the 1.1 T barium ferrite reactions, at Daresbury, which was not observed in the reactions in zero field or
0.2 T. This suggests that the magnetic field may influence the reaction pathway. The peak was identified as the (3 1 1) peak of magnetite (Fe₃O₄). When these reactions were repeated at the ESRF however, no such intermediate peak was observed (it would be at 6.56°). Peak assignment of the Fe₃O₄ intermediate is difficult because it is based on just one peak. Furthermore, peak assignment is complicated by the conversion of the data from energy to 2θ or d-spacing, and the fact that the high temperatures reached in the reaction are liable to affect the peak positions. It is possible that this transitory peak is not in fact due to an intermediate phase, but due to some other effect. Preferential orientation of crystals formed during the reaction (in a needle shape, or in a shiny fibre, for example) is one possible explanation for why a large peak would be seen. Another explanation for the large peak is crystallites moving in and out of the X-ray beam. These reactions were on powders where the particles would have greater freedom of movement compared to pellets.

Reaction timescales for the BaFe₁₂O₁₉ reactions were difficult to estimate. More runs for each reaction type are required in order to gain enough information on the transformation time from the reactants to the products, to say whether there are any trends from zero field to applied field.

Some of the barium ferrite reactions in zero field, 0.2 T and 1.1 T showed a curvature of their peak positions to higher energy or 2θ after the reaction had happened. This peak curvature is due to the high temperatures reached in SHS reactions. Most materials have a positive coefficient of thermal expansion. Raising the temperature of such a material causes its lattice to expand, while cooling leads to lattice contraction. Therefore the lattice of the SHS product should contract as it cools. Lattice contraction will be evident in the positions of the Bragg peaks in the diffraction patterns: if the d-spacing of the product gets smaller, the peaks will shift to higher energy or 2θ positions.

If the data is plotted in the format shown in Figure 5.18, shifting of the peaks to higher energy values can be seen. The data in Figure 5.18 is for the same 1.1 T
barium ferrite reaction as shown in Figure 5.8, Figure 5.10 and Figure 5.11. The lattice contraction can be quantified by following a particular peak, say the one at \( \sim 60 \text{ keV} \), and plotting the d-spacing of that peak in each scan relative to its d-spacing in the post-SHS product. This is shown in Figure 5.19 for a barium ferrite 1.1 T run, and shows that the initial d-spacings are \( \sim 2.5 \% \) larger than they are in the post-SHS product. The cooling rate of the product can be estimated from Figure 5.19. It shows that it takes 45-60 s for the lattice to contract to its final value. The peak positions were found manually by using the cursor on the Xfit program. This led to errors of \( \pm 0.1 \text{ keV} \) which for the 60 keV peak corresponds to \( \pm 0.004 \text{ Å} \).

![Graph showing lattice contraction over time](image)

**Figure 5.18** – \( \text{BaFe}_{12}\text{O}_{19} \) 1.1 T reaction, Daresbury July 99 data (middle detector), 250 ms per scan, 2 s between scans (2D plot of time vs. energy); (a) complete data set of 70 scans, (b) close-up showing curvature of peaks. This plot shows the curvature of peak positions towards higher energies, or smaller d-spacings, i.e. lattice contraction.
Figure 5.19 – Change in d-spacing vs. time for BaFe$_{12}$O$_{19}$ 1.1 T reaction, Daresbury July 99 data. This plot shows that the lattice takes ~45-60 s to contract to its final value after the SHS wave has passed.

An attempt was made to extract temperature information from the observed lattice contraction, using Eqn. 5.6 for the thermal expansion coefficient, $\alpha$,

$$\alpha = \frac{10^6 \Delta \ell}{\ell \Delta T}$$

Eqn. 5.6

where $\Delta \ell = \ell - \ell_0$, $\ell = $ d-spacing at temperature $T$, $\ell_0 = $ d-spacing in post-SHS product and $\Delta T = $ change in temperature. To calculate the change in temperature $\Delta T$ it was assumed that the peak followed to produce the $d/d_0$ plot (Figure 5.19) was that of Fe$_3$O$_4$, and the value of $\alpha$ was the same at all temperatures (although it is in fact a function of temperature). The thermal expansion coefficient $\alpha$ for Fe$_3$O$_4$ was found to be $8.46 \times 10^{-6}$ °C$^{-1}$ and substituted into Eqn. 5.6, but without the $10^{-6}$ factor as this was already included in Eqn. 5.6. This gave $\Delta T \approx 2800$ °C. The reaction temperatures measured by optical pyrometry or thermal imaging camera suggest $\Delta T \approx 1000$ °C, which corresponds to a change in d-spacing of about 0.8%. The melting point of Fe$_3$O$_4$ is 1594 °C, and assuming that it does not melt, since Bragg peaks are still observed, the temperature is likely...
to be less than 1594 °C. So, the reaction temperature may well be higher than
~1000 °C measured by optical pyrometry, but it might not be as high as ~2800 °C
estimated from lattice contraction. It should be remembered that temperature is
only one factor that affects the diffraction peak positions. The stoichiometry of the
compound is also likely to influence the d-spacings, hence the peak positions, and
therefore the temperatures estimated from the shift in peak positions.

High temperatures are known to have an effect on X-ray diffraction patterns. As
the temperature increases the atoms in the diffracting material vibrate more and
the cell expands. This leads to the planes being less well defined, which means the
Bragg condition is not met as perfectly, and hence the intensities of the diffracted
peaks are reduced. The Debye-Waller factor describes this intensity reduction of
Bragg diffraction peaks. It was observed in our experiments, see for example
Figure 5.13, and has been noted for other TRXRD studies of SHS.\textsuperscript{86}

5.4.3 Fe/Fe\textsubscript{2}O\textsubscript{3} and BaFe\textsubscript{12}O\textsubscript{19}

Intermediates were observed for the zero field reactions on the Fe/Fe\textsubscript{2}O\textsubscript{3} system,
and for the 1.1 T reactions on the BaFe\textsubscript{12}O\textsubscript{19} system. The intermediate for the
Fe/Fe\textsubscript{2}O\textsubscript{3} system was identified as Fe\textsubscript{1+x}O, and for the BaFe\textsubscript{12}O\textsubscript{19} system it was
Fe\textsubscript{3}O\textsubscript{4}. The diffraction rings became spotty in the Fe/Fe\textsubscript{2}O\textsubscript{3} reactions, but not in
the BaFe\textsubscript{12}O\textsubscript{19} reactions. Lattice contraction was observed in some BaFe\textsubscript{12}O\textsubscript{19}
reactions, but not for Fe/Fe\textsubscript{2}O\textsubscript{3}.

5.4.4 Reaction timescales

The estimates of the reaction timescales cover a wide range of values and they do
not appear to follow any trends (see Table 5.6). There are various possible reasons
for this. One explanation is that there were differences in what was measured –
different volumes of the mixture were sampled in zero field compared to applied
field, and at the ESRF compared to Daresbury; different oxygen flow rates were
used; as well as variations between samples. Also, there is some doubt over what
the "reaction" is. Here it has been called the "transformation from the reactants to
the products", but this is not necessarily a simple process. Other processes such as
melting and recrystallisation are also likely. In Chapter 1 (Section 1.2.1) the
mechanisms of SHS were discussed, and in the non-equilibrium mechanism, crystallisation and recrystallisation processes take place after the chemical reaction is over. The time for the chemical reaction is there described as the time taken to go from the reactants to the amorphous product. This complicates the estimation of reaction timescales.

The direction of the SHS wave propagation relative to the X-ray beam for reactions on powders is different in zero field compared to applied field. In zero field the wave travels perpendicular to the X-ray beam, so the timescale information is related in a straightforward way to the reaction wavefront velocity. In a magnetic field however, the wave does not move in a well-defined direction relative to the X-ray beam, due to experimental constraints. A solution to this problem is to perform the reactions on pellets rather than powders.

The SHS wave in reacting pellets travels perpendicular to the X-ray beam, for both zero and applied field reactions. In applied fields however, there is the further consideration of the wave direction relative to the magnetic field. Depending on where the pellet is ignited, the wave may travel parallel to the field, perpendicular to the field, or at any orientation in between (though in all cases the wave direction is perpendicular to the X-ray beam). To gain reproducible timescales, several repeat pellet reactions should be performed, with some way of controlling the point of initiation so that the wave always travels in the same direction relative to the field. It would be interesting to obtain timescales for waves travelling parallel and perpendicular to the field. In Chapter 1 (Section 1.5.1) reactions on pellets of ferromagnetic intermetallic systems were described; a magnetic field perpendicular to the wave direction did not affect the reaction velocity, but the experiment with the field parallel to the wave direction had not been reported. The ESRF is the best place to get timescale information, because it has the better time resolution.

5.4.5 Reproducibility
There are certain factors which may influence the reproducibility of these reactions. One factor is the degree of homogeneity of the green mixture.
Inhomogeneities could arise due to poor mixing of the starting materials, or (for magnetic field reactions) due to the magnetic field causing a separation of the different components, due to their differing magnetic susceptibilities. The beam spot size is small so would be able to pick up on local inhomogeneities within the sample. However, the homogeneity checks performed confirmed that the green mixture was homogeneous (at least on the scale of a 0.5 mm diameter spot) and that it does not separate in a magnetic field. Another factor that may affect reproducibility is the movement of the material in the magnetic field. The pellet reactions were designed to minimise this potential source of irreproducibility, by pressing the green mixture into a compact. The pellet itself had to be kept in the same position relative to the field, although it was difficult to immobilise the pellet whilst ensuring it would still ignite and propagate. The material chosen to keep the pellet in place had to have a low thermal conductivity to avoid taking heat away from the reaction and stopping the propagation. A third factor is the nature of SHS reactions – are they by nature reproducible, or is some variation inevitable? This depends on the scale on which the reactions are observed. On the macroscopic scale the reactions proceed in a reproducible way, but the products formed may not be reproducible. For example, post-SHS products from the reaction of \( \text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 + \text{O}_2 \) in a magnetic field contain shiny and matt parts. These are distributed throughout the pellet or powder product in an irregular manner, which may lead to variation of the results from one run to the next.

5.4.6 Pellet reactions

A development in the way these reactions were performed was to use compacted pellets of green mixture, rather than powders. This was for a number of reasons. Firstly, there was concern that the magnetic field may lead to inhomogeneity of the green mixture powder. Secondly, in a powder the components are free to move around during the reaction; movement might be expected in a magnetic field. This could lead to results which are not reproducible from one run to the next. Thirdly, the direction taken by the SHS propagation wave is more well defined in pellets compared to powders. In magnetic field reactions the wave direction is poorly defined for powders, so conducting reactions in pellets in magnetic fields has the advantage of a well-defined wave direction, important for timescale calculations.
Fourthly, by performing reactions on pellets there are more similarities between reactions in zero and applied fields; the green mixtures have the same shape and density.

The green mixture powder did not separate in the magnetic field; neither did pellets of green mixture. Pellets were hoped to improve the reproducibility between runs, and reactions with pellets were found to be reproducible. The timescales should be more accurate for the pellet reactions, although this was not observed. There are difficulties with performing reactions on pellets – pellets are more difficult to set up and ignite, and the density of the pellet may lead to reduced intensities or noise. Once the procedure is sorted out and runs smoothly, pellets should be the best way of performing TRXRD on SHS reactions.

5.4.7 Effect of a magnetic field as observed by TRXRD

A magnetic field has been seen to affect SHS reactions, by TRXRD. For Fe/Fe₂O₃ the zero field reactions appear different to the 0.2 T and 1.1 T reactions. The 0.2 T reactions have diffraction rings which are more “spotty” and the products contain more Fe₁₋ₓO and Fe₃O₄ than their zero field counterparts. In the zero field reactions, Fe₁₋ₓO is observed as an intermediate phase. For BaFe₁₂O₁₉ the reaction appears to proceed differently in zero field, 0.2 T and 1.1 T. The 1.1 T results taken at Daresbury show a large peak, which is possibly an intermediate phase, and was not observed in the zero field reactions. If this was an intermediate, it would suggest that the magnetic field was affecting the combustion. If the peak is in fact something else, say preferential orientation, it still suggests that the magnetic field is affecting the reaction.

The precise effect of a magnetic field on SHS is however unclear from these TRXRD studies. Several repeat runs under each set of reaction conditions and an improved experimental set-up (using pellets, for example) would be required to come to any firm conclusions about the influence of a magnetic field on the reactions themselves.

193
5.4.8 ESRF vs. Daresbury

The results from ESRF and Daresbury were not always in agreement. The reasons for this are unclear, although it may be due to inherent irreproducibility from one run to the next. Most of the results reported in this chapter are from the ESRF, because the quality of data was better than from Daresbury.

5.5 Conclusions

This chapter has shown that time-resolved X-ray diffraction is a useful way to study SHS reactions of ferrite systems. These were the first TRXRD studies of SHS reactions to form ferrites, and the first such studies of reactions in magnetic fields. They were also the first TRXRD studies of SHS reactions to use an energy-dispersive set-up. As a result of these experiments the best procedure for TRXRD studies of these reactions has been established, and the important variables have been identified. These include the amount of green mixture used and the amount sampled by the beam, the direction of the propagation wave relative to the beam, and the use of pressed pellets of green mixture to minimise the differences between the zero and applied field reactions.

Reactions of Fe + Fe2O3 and BaO2 + Fe + Fe2O3 in the presence of oxygen were investigated. The reaction pathways were observed, and differences were seen between reactions in zero field and in magnetic fields of 0.2 T and 1.1 T. A wüstit (Fe1-xO) intermediate was observed for reactions of Fe/Fe2O3 in zero field, persisting for 6-12 s. A magnetite (Fe3O4) intermediate was observed for reactions of the BaFe12O19 system in a magnetic field of 1.1 T, lasting for ~9 s. Curvature of the diffraction peaks towards higher energies revealed lattice contraction after the passage of the SHS wave. For a 1.1 T barium ferrite reaction, the lattice contracted by about 2.5 % in about 60 s after the passage of the SHS wave. The temperature was estimated to reach ~2800 °C, although this value should be treated with caution.
The results presented in this chapter hint at the wealth of information that can be obtained from TRXRD studies of SHS reactions. There is much scope for future work; some suggestions are given below.

First, more data is required to obtain more reproducible results. The table of experiments performed, Table 5.1, shows that there are experiments still to do. In particular, ESRF experiments should be performed on pellets in zero field, 0.2 T and 1.1 T. Several runs per reaction type should be performed.

Secondly, the way the reactions are done could be improved. Performing reactions on pellets ensures similar conditions in zero field as applied field and that the wave travels in a well-defined direction relative to the X-ray beam. Controlling the wave direction relative to the magnetic field is also important. The reactions could be quenched and the samples analysed by techniques such as SEM and XRD, in order to aid the identification of any intermediate phases produced. Single X-ray diffraction patterns could be taken of the post-SHS product at various points across its surface, to investigate the distribution of phases and whether this changes under the influence of a magnetic field. Infra red thermography could be used to correlate the reaction temperature with the diffraction data, as has been done for other SHS studies.\textsuperscript{86,87} The reactions themselves could be ignited in bulk in a furnace, rather than at a point. For example, the green mixture pellet could be heated slowly in a furnace, allowing longer X-ray exposure times, to see phase transformations as a function of temperature.

Thirdly, more information could be obtained from the TRXRD data. Rietveld analysis is a powerful tool which could be used to quantify the amounts of each phase in any one diffraction pattern (scan), and thus build up a plot of the relative amounts of each phase vs. time. It would give a plot similar to that shown in Figure 5.16 for the wüstite intermediate, except it would be a quantitative, rather than qualitative, plot. It would provide more definitive information about the existence and duration of any intermediate phases. The diffraction rings give
information on processes during the reaction, particularly the formation of large crystallites. Identifying which phases form these large crystals, and their Miller indices, and correlating the appearance of the spotty rings with time, may give clues to the processes that are happening in the SHS reactions. Lattice contraction is another area with potential. In this chapter, the lattice contraction has been reported for just one reaction. If the peak positions for each scan in a run could be easily traced, the degree of lattice contraction could be measured, and the reaction temperature estimated. That could be compared with infra red thermography measurements to check the accuracy of the estimated temperature and to estimate cooling rates.

Fourthly, TRXRD studies could be extended to other systems, such as reactions on non-ferromagnetic systems. For example, the reactions studied in high magnetic fields at Nijmegen (Chapter 4), BaTiO₃ and SrTiO₃, could be studied by TRXRD to see if the magnetic field has any influence on the reaction pathways in these systems.
6 Conclusions

The aim of this project was to understand how applied magnetic fields influence self propagating high temperature synthesis (SHS) reactions to form ferrites. The objective was to learn how to control the microstructure and magnetic properties of the product by controlling the reaction conditions. To achieve this aim, experiments were performed to investigate what happens when SHS reactions are conducted in a magnetic field, and to try to understand why those things happen. The main conclusions from this project are described below.

The effects of a magnetic field on the SHS reaction of \( \text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 \) in the presence of oxygen have been determined. A magnetic field leads to hotter and faster reactions, a greater degree of conversion of the reactants, a needle-like microstructure in the post-SHS product, and a reduced coercive field in the annealed product. The results described in Chapter 4 showed that in a field of 1.1 T the reactions of \( \text{BaO}_2 + \text{Fe} + \text{Fe}_2\text{O}_3 \) under a flow of oxygen were about 200 °C hotter than in zero field. The products from the applied field synthesis contained fused, shiny parts and brown coloured matt parts. Mössbauer spectroscopy and X-ray diffraction showed that the shiny parts were more fully combusted than the matt parts or the zero field products. They contained less unreacted starting materials and more of the combusted products such as \( \text{Fe}_3\text{O}_4 \) and \( \text{BaFe}_2\text{O}_4 \). Electron microprobe analysis revealed needle shaped regions in the post-SHS applied field (AF) product which were not seen in the zero field (ZF) product. The influence of the field remained even after annealing; the annealed \( \text{BaFe}_{12}\text{O}_{19} \) products showed a 20-30 % reduction in coercive field when made in a magnetic field.

Studies of the influence of processing parameters on the reactions revealed that oxygen accessibility is a crucial factor. The oxygen flow rate and the source of oxygen had a marked effect on the properties of the products. As the oxygen flow rate was increased from 0 to 10 l min\(^{-1}\), the reactions were hotter and faster, and the amount of the more fully combusted shiny part in the AF product increased, as
described in Chapter 3. Sodium perchlorate was used as an alternative source of oxygen, acting as an internal oxidising agent. As the oxygen source was changed from air to oxygen to sodium perchlorate, the reactions were found to be hotter and faster, the post-SHS products were more fully converted, and the annealed products exhibited lower coercive fields. As an internal source of oxygen the perchlorate provides better oxygen accessibility to the reaction than an external oxygen flow.

The influence of the magnetic field compared to zero field was also found to depend on the oxygen source that was used. When perchlorate was used, the ZF and AF reactions and products were similar in nature, having similar reaction temperatures, reaction completeness and microstructures. A reduction in the coercive field of the AF product was noted compared to the ZF product, although the magnitude of the reduction was less than for the non-perchlorate products, ~100 Oe compared to ~400 Oe.

There is a correlation between the temperature reached in the SHS reaction, the microstructure and reaction completeness of the post-SHS product and the magnetic parameters of the annealed product. Higher reaction temperatures appear to be responsible for the greater degree of conversion of the reactants and the needle-like microstructure of the post-SHS product, and the reduction in coercive field of the annealed product. Higher reaction temperatures were observed for AF compared to ZF reactions with an external oxygen flow, and for both ZF and AF reactions where sodium perchlorate was used as an internal oxidising agent compared to reactions with an external oxygen flow. Higher temperatures promote solid state reactions, which leads to more fully combusted products. The needle-like microstructure may be due to melting and nucleation processes occurring at the elevated temperatures. The coercive field reduction was attributed to the improved combustion leading to fewer pinning centres in the post-SHS and annealed products.
Control of the magnetic properties of the ferrite products appears to be possible by controlling the reaction conditions. By grouping the products into the categories of non-perchlorate ZF and matt parts, non-perchlorate shiny parts, perchlorate powder and perchlorate bar, different groupings of coercive field and maximum magnetisation values were observed. This offers the potential to control the coercivity of $\text{BaFe}_{12}\text{O}_{19}$ by choice of SHS reaction conditions, rather than by chemical doping.

Time resolved X-ray diffraction has been shown to be a technique that can provide useful information on the processes occurring in SHS. The best procedure to perform TRXRD studies of these reactions has been established from the experiments described in Chapter 5. Reactions should be performed on pellets, the amount of green mixture used and the amount sampled by the X-ray beam must be controlled, as should the direction of the propagation wave relative to the beam. Reaction pathways for the Fe/Fe$_2$O$_3$ and BaFe$_{12}$O$_{19}$ reactions were observed and differences were seen between the reactions in zero field and in magnetic fields of 0.2 T and 1.1 T. Intermediate phases were observed during some reactions. A wüstite ($\text{Fe}_{1-x}\text{O}$) intermediate was seen in the zero field Fe/Fe$_2$O$_3$ reactions, while a magnetite ($\text{Fe}_3\text{O}_4$) intermediate was seen in some 1.1 T BaFe$_{12}$O$_{19}$ reactions. The transformation times from reactants to products were also estimated. Lattice contraction was observed of ~2.5% in 60 s after the passage of the SHS wave. TRXRD is a route to gaining detailed information on reaction processes and now that the best procedure is in place, a wealth of information may be obtained from such studies. For example, more reliable timescale estimates could be found, and Rietveld analysis could be used to determine the concentration profiles of the different phases against time.

The mechanism by which the magnetic field influences the reactions has been investigated. Experiments on pre-aligned green mixtures, and reactions in high magnetic fields on strongly and weakly magnetic systems, have provided evidence that reorganisation of the green mixture along the field lines is one way in which the field acts. Reactions on pellets in high magnetic fields have provided evidence
that the field also acts in other ways; possible mechanisms are that paramagnetic oxygen is attracted into the magnetic field, or that the field acts on ions at the SHS wavefront. It may be possible to distinguish between these two hypotheses by performing SHS reactions on systems that do not involve oxygen. Such experiments should provide further valuable information on why a magnetic field affects SHS reactions.
References


28 London and Scandinavia Metallurgical Co. website: [http://www.lsm.co.uk](http://www.lsm.co.uk).


73 PC-APD v. 4.0b, © Philips Electronics N.V. 1994.
76 Unit Cell, © Tim Holland and Simon Redfern 1995.
97 L. Smart, Open University Solid-State Chemistry study book, for Block 8 of S343 Inorganic Chemistry course, The Open University, Milton Keynes, 1992, p.43.


ASAD (All Singing All Dancing), by Andrew Jupe, Birkbeck College, London.

PGPlot by T. J. Pearson © California Institute of Technology 1988-1997, accessed via the xrdsv1 computer at Daresbury Laboratory.

UNIMAP, part of the UNIRAS suite of programs, accessed via the xrdsv1 computer at Daresbury Laboratory.

Korcake.sh program, available from ESRF, for details see their website: [http://www.esrf.fr/exp_facilities/ID11/handbook](http://www.esrf.fr/exp_facilities/ID11/handbook), data acquisition and reduction section. MI517cake.sh was a modified version of this program to process the data from the SHS runs rather than single scans.


Publications


7. I. P. Parkin, Q. A. Pankhurst, L. Affleck, M. D. Aguas, M. V. Kuznetsov, “Self-propagating high temperature synthesis of BaFe$_{12}$O$_{39}$, Mg$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Li$_{0.5}$Fe$_2$O$_4$; time resolved X-ray diffraction studies (TRXRD)”, *J. Mater. Chem.*, 2001, 11, 193-199.

Published abstracts


Presentations (talks)

June 1999
Condensed Matter Group Graduate Review, UCL, Physics Dept.
• "Self-propagating High Temperature Synthesis of Magnetic Materials"

November 1999
Inorganic Chemistry Group Seminar, UCL, Chemistry Dept.
• "Self-propagating High Temperature Synthesis of Barium Ferrite"

November 1999
Highlights of Physics Research and R&D by Younger Physicists, Rutherford Appleton Laboratory.
• "Studying SHS Reactions by Time-Resolved X-ray Diffraction"

December 1999
CMMP 99, Leicester University.
• "Time-Resolved X-ray Diffraction Studies of Solid State Combustion Reactions"

June 2000
CIMTEC conference on Mass and Charge Transport in Inorganic Materials, Italy (Venice).
• "Combustion Synthesis of Ferrite Magnets"

June 2000
Glaxo Wellcome Travel Awards, UCL, Chemistry Dept.
• "Self-propagating High Temperature Synthesis of Magnetic Materials"

June 2000
Condensed Matter Group Graduate Review, UCL, Physics Dept.
• "Self-propagating High Temperature Synthesis of Magnetic Materials"

September 2000
8th International Conference on Ferrites, Japan (Kyoto).
• "Combustion Synthesis of Hexagonal and Spinel Ferrites; Effect of Applied Magnetic Fields on Microstructure and Bulk Magnetic Properties"

November 2000
Inorganic Chemistry Group Seminar, UCL, Chemistry Dept.
• "Self-propagating High Temperature Synthesis of Barium Ferrite"

June 2001
Condensed Matter group seminar series, UCL, Physics Dept.
• "Self Propagating High Temperature Synthesis of Ferrites in Magnetic Fields"

June 2001
Ramsay Medal talk, UCL, Chemistry Dept.
• "Self Propagating High Temperature Synthesis of Ferrites in Magnetic Fields"

July 2001
ASPIIC talk, Queen Mary and Westfield College, London.
• "Self Propagating High Temperature Synthesis of Ferrites in Magnetic Fields"

July 2001
RSC Young Researchers' Award talk, RSC Annual Conference, ICC, Birmingham.
• "Time-Resolved X-ray Diffraction Studies of Self-Propagating Reactions"

Presentations (posters)

November 1999
Meeting of students in the Advanced Magnetics Programme, Seagate Ltd, Londonderry.
• "Self-propagating High Temperature Synthesis of Barium Ferrite"

November 1999
Highlights of Physics Research and R&D by Younger Physicists, Rutherford Appleton Laboratory.
• "Studying SHS reactions by Time-Resolved X-ray Diffraction"

June 2000
Second year PhD posters, UCL, Chemistry Dept.
• "Self-propagating High Temperature Synthesis of Barium Ferrite"

May 2001
Current Research in Magnetism meeting, Rutherford Appleton Laboratory.
• "Self-propagating High-temperature Synthesis of Composite Magnetically Hard-Soft Ferrites"

July 2001
5th International Conference on Materials Chemistry, Bangor.
• "Time-Resolved X-Ray Diffraction Studies of Self-Propagating Reactions"

July 2001
RSC Annual Conference, ICC, Birmingham.
• "Time-Resolved X-Ray Diffraction Studies of Self-Propagating Reactions"