به نام خدا

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Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics

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A B S T R A C T
Since their discovery in the 1950s there has been an increasing degree of interest in the hexagonal ferrites, also known as hexaferrites, which is still growing exponentially today. These have become massively important materials commercially and technologically, accounting for the bulk of the total magnetic materials manufactured globally, and they have a multitude of uses and applications. As well as their use as permanent magnets, common applications are as magnetic recording and data storage materials, and as components in electrical devices, particularly those operating at microwave/GHz frequencies. The important members of the hexaferrite family are shown below, where Me = a small 2+ ion such as cobalt, nickel or zinc, and Ba can be substituted by Sr:

- M-type ferrites, such as BaFe_{12}O_{19} (BaM or barium ferrite), SrFe_{12}O_{19} (SrM or strontium ferrite), and cobalt–titanium substituted M ferrite, Sr– or BaFe_{12−2x}Co_{x}Ti_{x}O_{19} (CoTiM).
- Z-type ferrites (Ba_{3}Me_{2}Fe_{24}O_{41}) such as Ba_{3}Co_{2}Fe_{24}O_{41}, or Co_{3}Z.
- Y-type ferrites (Ba_{3}Me_{2}Fe_{24}O_{42}), such as Ba_{3}Co_{2}Fe_{16}O_{42}, or Co_{3}Y.
- W-type ferrites (BaMe_{2}Fe_{16}O_{27}), such as BaCo_{2}Fe_{16}O_{27}, or Co_{2}W.
- X-type ferrites (BaMe_{2}Fe_{28}O_{46}), such as Ba_{2}Co_{2}Fe_{28}O_{46}, or Co_{2}X.
- U-type ferrites (BaMe_{2}Fe_{30}O_{60}), such as Ba_{4}Co_{2}Fe_{30}O_{60}, or Co_{2}U.

The best known hexagonal ferrites are those containing barium and cobalt as divalent cations, but many variations of these and hexaferrites containing other cations (substituted or doped) will also be discussed, especially M, W, Z and Y ferrites containing strontium, zinc, nickel and magnesium. The hexagonal ferrites are all ferrimagnetic materials, and their magnetic properties are...
intrinsically linked to their crystalline structures. They all have a magnetocrystalline anisotropy (MCA), that is the induced magnetisation has a preferred orientation within the crystal structure. They can be divided into two main groups: those with an easy axis of magnetisation, the uniaxial hexaferrites, and those with an easy plane (or cone) of magnetisation, known as the ferroxplana or hexaplana ferrites. The structure, synthesis, solid state chemistry and magnetic properties of the ferrites shall be discussed here. This review will focus on the synthesis and properties of bulk ceramic ferrites. This is because the depth of research into thin film hexaferrites is enough for a review of its own.

There has been an explosion of interest in hexaferrites in the last decade for more exotic applications. This is particularly true as electronic components for mobile and wireless communications at microwave/GHz frequencies, electromagnetic wave absorbers for EMC, RAM and stealth technologies (especially the X and U ferrites), and as composite materials. There is also a clear recent interest in nanotechnology, the development of nanofibres and fibre orientation and alignment effects in hexaferrite fibres, and composites with carbon nanotubes (CNT). One of the most exciting developments has been the discovery of single phase magnetoelectric/multiferroic hexaferrites, firstly Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$ Y ferrite at cryogenic temperatures, and now Sr$_3$Co$_2$Fe$_{24}$O$_{41}$ Z ferrite at room temperature. Several M, Y, Z and U ferrites have now been characterised as room temperature multiferroics, and are discussed here. Current developments in all these key areas will be discussed in detail in Sections 7–11 of this review, and for this reason now is the appropriate time for a fresh and critical appraisal of the synthesis, properties and applications of hexagonal ferrites.

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Contents

Note on magnetic units, conversion factors and hysteresis loops .............................................. 1194
1. Introduction ...................................................................................................................... 1196
2. The discovery, composition and characteristics of the hexagonal ferrites ............................... 1198
   2.1. The M ferrites ........................................................................................................... 1199
   2.2. The W ferrites ......................................................................................................... 1200
   2.3. The X ferrites ......................................................................................................... 1200
   2.4. The Y ferrites ......................................................................................................... 1200
   2.5. The Z ferrites ......................................................................................................... 1200
   2.6. The U ferrites ......................................................................................................... 1201
   2.7. Other hexagonal ferrites ......................................................................................... 1201
3. The structure of the hexagonal ferrites...................................................................................... 1201
   3.1. The spinel-based model .......................................................................................... 1202
   3.2. The S, R and T blocks ............................................................................................ 1204
   3.3. The M structure ...................................................................................................... 1207
   3.4. The W structure ...................................................................................................... 1207
   3.5. The X structure ...................................................................................................... 1208
   3.6. The Y structure ...................................................................................................... 1208
   3.7. The Z structure ...................................................................................................... 1210
   3.8. The U structure ...................................................................................................... 1210
   3.9. The structures of higher hexagonal ferrites ............................................................. 1210
   3.10. Electrical conductivity of ferrites ........................................................................ 1211
   3.11. Iron oxides ............................................................................................................ 1213
4. Synthesis methods for hexagonal ferrites.................................................................................. 1213
   4.1. Standard ceramic techniques ................................................................................... 1214
5. The solid state chemistry of the hexagonal ferrites ..................................... 1220
   5.1. BaM ferrite ........................................................................ 1222
   5.1.1. Coprecipitated BaM ................................................... 1223
   5.1.2. Salt-melt process for BaM ........................................... 1225
   5.1.3. Sol–gel synthesis of BaM ........................................... 1225
   5.1.4. Hydrothermal synthesis of BaM .................................. 1227
   5.1.5. Other synthesis methods for BaM ................................ 1229
   5.2. Other M ferrites ................................................................ 1232
   5.3. Substituted M ferrite ........................................................... 1234
   5.4. Y ferrite ........................................................................... 1237
   5.5. Z ferrite ........................................................................... 1238
   5.6. W ferrite ........................................................................... 1242
   5.7. X ferrite ........................................................................... 1243
   5.8. U ferrite ........................................................................... 1244
   5.9. Sintering aids .................................................................... 1246
   5.10. Grain growth in hexagonal ferrites ....................................... 1247
   5.11. Grain growth inhibitors .................................................... 1247
6. Magnetic properties of hexagonal ferrites .................................................... 1248
   6.1. Magnetism in hexagonal ferrites .......................................... 1248
   6.1.1. Magnetic moments and superexchange in the hexagonal ferrites 1249
   6.1.2. Summary of magnetic properties of hexagonal ferrites ........ 1251
   6.2. BaM ferrite ..................................................................... 1252
   6.2.1. Magnetically oriented BaM .......................................... 1255
   6.2.2. Substituted BaM ........................................................... 1255
   6.3. SrM ferrite ...................................................................... 1258
   6.3.1. Substituted SrM ............................................................. 1259
   6.4. PbM ferrite ...................................................................... 1260
   6.5. Co–Ti substituted M ferrites ............................................... 1260
   6.6. Other substituted M ferrites ............................................... 1261
   6.7. Y ferrites ........................................................................... 1263
   6.7.1. Substituted Y ferrites ..................................................... 1264
   6.8. Z ferrites ........................................................................... 1265
   6.8.1. Substituted Z ferrites ..................................................... 1267
   6.9. W ferrites ........................................................................... 1269
   6.9.1. Substituted W ferrites ..................................................... 1270
   6.10. X ferrites ........................................................................... 1271
   6.11. U ferrites ........................................................................... 1272
7. The microwave properties of hexagonal ferrites ......................................... 1273
   7.1. A brief theory of microwave resonance and losses in ferrites .... 1273
   7.1.1. Ferromagnetic resonance (FMR) .................................... 1274
   7.2. M ferrites ........................................................................... 1275
   7.3. CoTiM ferrites ................................................................. 1275
   7.4. Y ferrite ........................................................................... 1276
   7.5. Z ferrite ........................................................................... 1277
   7.6. W ferrite ........................................................................... 1278
   7.7. U ferrite ........................................................................... 1279
   7.8. X ferrite ........................................................................... 1279
Note on magnetic units, conversion factors and hysteresis loops

There exists a real confusion in the literature, with several different systems of units being used even today. The most common system in the literature is CGS (centimetre-gram-second system), and this is still used by many authors today, even though the accepted international standard has been the SI system for decades now. All values in this text have been converted to SI units, but some figures used may have CGS units.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>CGS unit</th>
<th>Conversion factor to SI</th>
<th>SI unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic induction/flux density</td>
<td>B</td>
<td>G</td>
<td>$10^{-4}$</td>
<td>T</td>
</tr>
<tr>
<td>Magnetic field strength/force</td>
<td>H</td>
<td>Oe</td>
<td>$10^{3}/4\pi (=79.58)$</td>
<td>A m$^{-1}$</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>m</td>
<td>emu</td>
<td>$10^{-3}$</td>
<td>A m$^{2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>erg G$^{-1}$</td>
<td>$10^{-3}$</td>
<td>J T$^{-1}$</td>
</tr>
<tr>
<td>Magnetisation (mass)</td>
<td>M, $\sigma$</td>
<td>emu g$^{-1}$</td>
<td>1</td>
<td>A m$^2$kg$^{-1}$</td>
</tr>
<tr>
<td>Volume magnetisation</td>
<td>M</td>
<td>emu cm$^{-3}$</td>
<td>10</td>
<td>A m$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4\pi M$</td>
<td>$10^{3}/4\pi$</td>
<td>A m$^{-1}$</td>
</tr>
<tr>
<td>Energy product/anisotropy const.</td>
<td>W, K</td>
<td>erg cm$^{-3}$</td>
<td>0.1</td>
<td>J m$^{-3}$</td>
</tr>
<tr>
<td>Magnetic flux</td>
<td>$\Phi$</td>
<td>Mx</td>
<td>$10^{-8}$</td>
<td>Wb</td>
</tr>
<tr>
<td></td>
<td></td>
<td>G cm$^{2}$</td>
<td>$10^{-8}$</td>
<td>V s</td>
</tr>
</tbody>
</table>

$M_s$ is the maximum magnetisation obtained in a sample when it is saturated by the applied magnetic field, and does not increase with a larger applied field. It has units of A m$^2$ kg$^{-1}$ (=1 emu g$^{-1}$), the same as magnetisation. If a plot is made of the measurement of magnetisation (M) against applied magnetic field (either B or H), $M_s$ will be the maximum magnetisation value obtainable for a sample. If a reverse field is applied, the magnetisation will at some point be reduced to zero, and then increase to a maximum of $-M_s$ again in the other direction. In ferro- or ferrimagnetic materials, the magnetisation will not pass through the origin however, and a symmetric ferroic hysteresis loop, or M–H loop, is formed. As the M–H loop does not pass through the origin, at zero applied field the material will still...
**Nomenclature**

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \varepsilon$</td>
<td>magnetocapacitance, change in $\varepsilon$ with B as a %</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>relative permittivity ($\varepsilon =$ permittivity, or dielectric constant)</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>$\mu_t$</td>
<td>relative permeability ($\mu =$ magnetic permeability)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density, in g cm$^{-3}$</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>B</td>
<td>applied magnetic field (flux density), in SI units of T</td>
</tr>
<tr>
<td>BaM</td>
<td>BaFe$<em>{12}$O$</em>{19}$ ferrite</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>Co$_2$Z, etc.</td>
<td>Co-containing hexaferrites, e.g. Ba$<em>3$Co$<em>2$Fe$</em>{24}$O$</em>{41}$ = Co$_2$Z, Ba$<em>2$Co$<em>2$Fe$</em>{12}$O$</em>{22}$ = Co$_2$Y</td>
</tr>
<tr>
<td>dB</td>
<td>decibel, a logarithmic unit, that when negative indicates a relative reduction</td>
</tr>
<tr>
<td>DGG</td>
<td>discontinuous grain growth, also known as exaggerated grain growth</td>
</tr>
<tr>
<td>EM</td>
<td>electromagnetic</td>
</tr>
<tr>
<td>emu</td>
<td>electromagnetic unit, CGS unit of magnetic dipole moment, equal to erg g$^{-1}$</td>
</tr>
<tr>
<td>erg</td>
<td>CGS unit of energy, equal to 10$^{-7}$ J, sometimes used for anisotropy constants</td>
</tr>
<tr>
<td>FMR</td>
<td>ferromagnetic resonance</td>
</tr>
<tr>
<td>$f_r$</td>
<td>resonant frequency at which FMR occurs</td>
</tr>
<tr>
<td>G</td>
<td>gauss, CGS unit of magnetic flux</td>
</tr>
<tr>
<td>H</td>
<td>magnetic field strength, in SI units of A m$^{-1}$</td>
</tr>
<tr>
<td>$H_A$</td>
<td>magnetic anisotropy field, in SI units of A m$^{-1}$</td>
</tr>
<tr>
<td>$H_c$</td>
<td>coercivity, in SI units of A m$^{-1}$</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high-resolution transmission electron microscope</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
</tr>
<tr>
<td>$K_1$, $K_2$, $K_3$</td>
<td>first, second and third order magnetic anisotropy constants, in SI units of J m$^{-3}$</td>
</tr>
<tr>
<td>LOA</td>
<td>list of acronyms</td>
</tr>
<tr>
<td>M</td>
<td>BaFe$<em>{12}$O$</em>{19}$ or SrFe$<em>{12}$O$</em>{19}$ ferrite</td>
</tr>
<tr>
<td>MCA</td>
<td>magnetocrystalline anisotropy</td>
</tr>
<tr>
<td>Me</td>
<td>metal cation</td>
</tr>
<tr>
<td>ME</td>
<td>magnetoelectric</td>
</tr>
<tr>
<td>MF</td>
<td>multiferroic</td>
</tr>
<tr>
<td>M–H</td>
<td>magnetisation vs. applied magnetic field hysteresis loop plot</td>
</tr>
<tr>
<td>MFM</td>
<td>magnetic force microscopy</td>
</tr>
<tr>
<td>MP</td>
<td>melting point</td>
</tr>
<tr>
<td>$M_r$</td>
<td>remnant magnetisation, in SI units of A m$^2$ kg$^{-1}$</td>
</tr>
<tr>
<td>$M_s$</td>
<td>saturation magnetisation, in SI units of A m$^2$ kg$^{-1}$</td>
</tr>
<tr>
<td>MW</td>
<td>microwave</td>
</tr>
<tr>
<td>MWCNT</td>
<td>multi-walled carbon nanotube</td>
</tr>
<tr>
<td>Mx</td>
<td>Maxwell, CGS unit of magnetic flux</td>
</tr>
<tr>
<td>NC</td>
<td>nanocrystal</td>
</tr>
<tr>
<td>NP</td>
<td>nanoparticle</td>
</tr>
<tr>
<td>Oe</td>
<td>oersted, CGS unit of magnetic field strength</td>
</tr>
<tr>
<td>P</td>
<td>electrical polarisation, in $\mu$C m$^{-2}$</td>
</tr>
<tr>
<td>PFM</td>
<td>piezoresponse force microscopy</td>
</tr>
<tr>
<td>RAM</td>
<td>radar absorbing material</td>
</tr>
<tr>
<td>RE</td>
<td>rare earth metal</td>
</tr>
<tr>
<td>rf</td>
<td>radio frequency</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SQUID</td>
<td>superconducting quantum interference device</td>
</tr>
<tr>
<td>SrM</td>
<td>SrFe$<em>{12}$O$</em>{19}$ ferrite</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>T</td>
<td>tesla, SI unit of magnetic flux or field strength</td>
</tr>
</tbody>
</table>
retain a magnetisation value, and this is $M_r$, the remnant magnetisation (at $H = 0$), also in A m$^{-2}$ kg$^{-1}$. $H_c$ is a measure of the magnetic field that has to be applied in a reverse direction to “coerce” the remnant magnetisation back to zero (hence, it is called coercivity), and it is the H value when the hysteresis loop crosses zero M, in units of A m$^{-1}$. As this value is equivalent to the magnetic flux density of the magnet used to apply the field, $H_c$ is often reported in units of tesla (T) or gauss (G), as well as oersteds (Oe), where 1 T = 10,000 G = 10,000 Oe = 795,775 A m$^{-1}$. As the values of $H_c$ tend to be large in SI units, often units of kA m$^{-1}$ are used instead (1 T $\sim$ 796 kA m$^{-1}$).

A ferrite that has a high $H_c$ is known as a hard ferrite, and these typically have large $M_r$ values that are about 50% of $M_s$ in randomly oriented samples (i.e., the ratio of $M_r:M_s$ is $\sim$0.5). With oriented domains this $M_r$ value can increase towards 100% of the $M_s$ value, which results in a wide, “square” looking $M$–$H$ hysteresis loop, and these are sometimes called square ferrites. Ferrites with a low $H_c$ are known as soft ferrites, as they require only a small applied field to reduce their magnetisation to zero. As a result, they tend to have smaller $M_r$ values as the magnetisation is approaching zero already in zero applied field, and produce narrow $M$–$H$ hysteresis loops. These two kinds of ferrite both have very different, but also very important, applications.

1. Introduction

Ever since Neolithic man first used a piece of suspended lodestone to navigate, mankind has used magnetic materials of various kinds. However, it was not until the advent of electricity that the magnetic processes began to be understood. It is now known that lodestone is an iron ore, magnetite, which is one of a wide range of magnetic ceramics based on iron(III)oxide, called the ferrites. Magnetite, Fe$_3$O$_4$, is in a structural class of compounds known as the spinels with the composition $MeFe_2O_4$ where $Me$ is a divalent cation, $Fe^{2+}$ in the case of magnetite. These compounds have a cubic structure, but there are also a group of ferrites with a hexagonal crystal structure, also know as hexaferrites. These have become massively important materials commercially and technologically, with BaM hexaferrite alone accounting for 50% of the total magnetic materials manufactured globally, at over 300,000 tonnes per year, and they have a multitude of uses and applications [1].

As can be seen from Fig. 1, since their discovery in the 1950s there has been an exponentially increasing degree of interest in the hexagonal ferrites, which is still growing today. A record number of hexaferrite papers were published in 2011. As well as their general magnetic properties, uses as magnetic recording and data storage materials, and a constant awareness of their MW properties, there has been an explosion of interest in hexaferrites in the last decade for more exotic applications (Fig. 2). This is particularly true as MW/GHz electronic components and EM absorbers (RAM), and as composite materials. There is also a clear recent interest in nanotechnology and mixtures with CNTs, magnetoelectric/multiferroic applications, and the development of orientation and alignment effects in ferrite fibres, with a growth in articles on these themes in the last few years. Current developments in these key areas will be discussed in detail in Sections 7–11 of this review, and for these reasons now
Fig. 1. Yearly number of hexaferrites publications from 1959 to 2011 (search using Scopus).

Fig. 2. Yearly number of hexaferrites papers by specialised theme since 1975 (search using Scopus).
is the appropriate time for a fresh and critical appraisal of the synthesis, properties and applications of hexagonal ferrites.

For the purposes of this review the interest shall be focused upon the hexagonal ferrites containing barium and cobalt as divalent cations, although substituted or doped variations of these and ferrites containing other cations will also be discussed, especially M, W, Z and Y ferrites containing strontium, zinc, nickel and magnesium. When discussing the ferrites in general, the formula will be given with $\text{Ba}^{2+}$ as the large divalent cation and $\text{Me}^{2+}$ representing the smaller divalent cation (e.g., Z ferrite $= \text{Ba}_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}$), but the $\text{Ba}^{2+}$ can be replaced by $\text{Sr}^{2+}$, and often by $\text{Pb}^{2+}$, with no change in basic structure type. Unless otherwise stated, in this review assume that the large divalent ion will be $\text{Ba}^{2+}$ – if the ferrite is named $\text{Co}_2\text{Z}$ or $\text{Zn}_2\text{W}$ for instance, it will be barium. The hexagonal ferrites are all ferrimagnetic materials, and their magnetic properties are intrinsically linked to their crystalline structures. They all have a magnetocrystalline anisotropy (MCA), that is the induced magnetisation has a preferred orientation within the crystal structure, and they can be divided into two main groups, those with an easy axis of magnetisation, the uniaxial hexaferrites, and those with an easy plane (or cone) of magnetisation, known as the ferroxplana or hexaplana ferrites. Although the practical magnetic properties of the ferrites shall be discussed here, further details regarding their magnetic characteristics and the theory behind them can be found in the excellent review on microwave ferrites by Özgür et al. [1] This review will concentrate on the synthesis and properties of bulk ceramic ferrites. This is because the depth of research into thin film hexaferrites is enough for a review of its own.

2. The discovery, composition and characteristics of the hexagonal ferrites

The magnetic mineral magnetoplumbite was first described in 1925 [2], and in 1938 the crystal structure was deduced as being hexagonal with the composition $\text{PbFe}_{7.5}\text{Mn}_{3.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$ [3]. The synthetic form of magnetoplumbite was found to be $\text{PbFe}_{12}\text{O}_{19}$, or pure PbM, and a number of isomorphous compounds were suggested including $\text{BaFe}_{12}\text{O}_{19}$, although this material was not structurally investigated until after the Second World War, when Philips Laboratories led the way in developing ferrites under the direction of Snoek. $\text{BaFe}_{12}\text{O}_{19}$ is known by many names, including barium ferrite, hexaferrite, barium hexaferrite, ferroxdure, M ferrite and $\text{BaM}$, and was also shown to consist of a hexagonal structure by Went et al. [4]. Investigations of the $\text{BaO–Fe}_2\text{O}_3$ system by Wijn and Braun then produced more complex hexagonal compounds, in which there were both divalent and trivalent iron species ($\text{BaFe}_{18}\text{O}_{27}$) [5,6], and further compounds were also discovered by Jonker, Wijn and Braun when the ternary $\text{BaO–Fe}_2\text{O}_3–\text{MeO}$ system was heated at 1200–1400 °C, where $\text{Me} = a$ small divalent cation [7]. Detailed reports of all the main hexaferrite phases were published by Philips Laboratories in the 1950s, culminating in Smit and Wijn's excellent book “Ferrites”, published in 1959 [8]. $\text{BaM}$ and the cubic $\text{MeFe}_2\text{O}_4$ spinel appear as the end members of this system, with zero populations of $\text{Me}$ and $\text{Ba}$ respectively. The physical characteristics of $M$ ferrites and the cobalt-hexagonal ferrites, as categorised by their discoverers, are shown in Table 1.

All of these compounds were found to have a hexagonal crystal structure, with two crystalline lattice parameters: $a$, the width of the hexagonal plane, and $c$, the height of the crystal (Fig. 3). All had a

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Formula</th>
<th>Molecular mass (g)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$c$ (Å)</th>
<th>Magnetisation at room temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BaM}$</td>
<td>$\text{BaFe}<em>{12}\text{O}</em>{19}$</td>
<td>1112</td>
<td>5.28</td>
<td>23.18</td>
<td>uniaxial</td>
</tr>
<tr>
<td>$\text{SrM}$</td>
<td>$\text{SrFe}<em>{12}\text{O}</em>{19}$</td>
<td>1062</td>
<td>5.11</td>
<td>23.03</td>
<td>uniaxial</td>
</tr>
<tr>
<td>$\text{Co}_2\text{Y}$</td>
<td>$\text{Ba}<em>2\text{Co}<em>2\text{Fe}</em>{12}\text{O}</em>{22}$</td>
<td>1410</td>
<td>5.40</td>
<td>43.56</td>
<td>in plane</td>
</tr>
<tr>
<td>$\text{Co}_2\text{Z}$</td>
<td>$\text{Ba}<em>2\text{Co}<em>2\text{Fe}</em>{24}\text{O}</em>{41}$</td>
<td>2522</td>
<td>5.35</td>
<td>52.30</td>
<td>in plane</td>
</tr>
<tr>
<td>$\text{Co}_2\text{W}$</td>
<td>$\text{Ba}<em>2\text{Co}<em>2\text{Fe}</em>{16}\text{O}</em>{27}$</td>
<td>1577</td>
<td>5.31</td>
<td>32.84</td>
<td>in cone</td>
</tr>
<tr>
<td>$\text{Co}_2\text{X}$</td>
<td>$\text{Ba}<em>2\text{Co}<em>2\text{Fe}</em>{28}\text{O}</em>{46}$</td>
<td>2688</td>
<td>5.29</td>
<td>84.11</td>
<td>in cone</td>
</tr>
<tr>
<td>$\text{Co}_2\text{U}$</td>
<td>$\text{Ba}<em>4\text{Co}<em>2\text{Fe}</em>{16}\text{O}</em>{60}$</td>
<td>3624</td>
<td>5.31</td>
<td>38.16$^a$</td>
<td>in plane</td>
</tr>
</tbody>
</table>

$^a$ Note that here the $c$ parameter of $\text{Co}_2\text{U}$ is given for a unit cell that consists of only one molecular unit, as it was described in the past when Ref. [8] was written. These days it is more typically taken to be three molecular units, with a $c$ value three-times greater.
preferred direction of magnetisation when placed in a magnetic field, giving them an MCA, which was often parallel to the \( c \)-axis, coming out of the basal plane of the hexagonal crystal. This uniaxial anisotropy in effect fixes the magnetisation in the direction of the \( c \)-axis, and the magnetisation can only be moved out of this direction at the expense of the high anisotropic energy.

However, some compounds containing a divalent cation, especially those containing cobalt, were found to have a plane of spontaneous magnetisation in the basal plane, perpendicular to the \( c \)-axis. These compounds were named the ferroxplana ferrites, and are now known also to include compounds which have a cone of magnetisation at an angle \( 0 < \theta < 90^\circ \) to the \( c \)-axis. While the direction of magnetisation can easily rotate within the plane or cone through an angle of \( 360^\circ \), the magnetisation is still locked in this plane or cone by a high magnetic anisotropy energy.

### 2.1. The M ferrites

The compound BaM, \( \text{BaFe}_{12}\text{O}_{19} \), was known to exist for many years, with a melting point of 1390 °C confirmed in 1936 [9]. However, the structure was not confirmed as being isomorphous with the hexagonal magnetoplumbite until it was first studied and characterised magnetically in the early 1950s by Philips [4]. BaM was initially named ferroxdue, to distinguish it from the spinel ferrite which was named ferroxcube [10]. At the time it was considered an unusual ferrite as it contained no cobalt or nickel, yet it was magnetically hard, with a coercivity of 160–255 kA m\(^{-1}\). Although it had a lower saturation magnetisation than the existing alloy magnets, it was much cheaper to produce, had a high electrical resistivity of \( 10^8 \) Ω cm and the high magnetic uniaxial anisotropy along the \( c \)-axis [8]. The molecular mass of BaM is 1112 g and the maximum density is 5.295 g cm\(^{-3}\) [11], although in reality the ceramic material often has a density as low as 90% of theoretical density. The hardness of BaM in the \( c \)-axis has been calculated to be 5.9 GPa [12], and measured as 6.0 GPa [13].

SrM, in which the barium has been replaced by the smaller strontium atom, has a density of 5.101 g cm\(^{-3}\) [11] and molecular mass of 1062 g, but resembles BaM in most other physical properties [14]. The Pb\(^{2+}\) ion is sized in between Ba and Sr, but lead is a much heavier atom than barium, and so PbM has a molecular mass of 1181 g and a density of 5.708 g cm\(^{-3}\) [11]. Undoped CaM has never been seen as a pure phase, but it has been formed in glass by the glass crystallisation method [15]. A detailed study of the thermal properties of polycrystalline M ferrites has been made [16], and the values are shown in Table 2. The \( T_c \) values are lower than those published for single crystal ferrites, and were taken from peaks in the standard molar heat capacity plots.
2.2. The $W$ ferrites

$W$ ferrites have the formula $\text{BaMe}_2\text{Fe}_{16}\text{O}_{27}$, where Me is usually a first row transition metal or some other divalent cation, and the barium can be substituted by another group two metal. The first reported $W$ ferrite was $\text{Fe}_2\text{W}$ ($\text{BaFe}_2\text{Fe}_{16}\text{O}_{27}$) [4], but it was initially only made as a mixed phase with $M$ and $X$ ferrites. Single phase $\text{Fe}_2\text{W}$ was found to have an easy axis of magnetisation in the $c$-axis of the hexagonal crystal structure, but had a much higher electrical conductivity than $\text{BaM}$ due to the $\text{Fe}^{2+}$ ions. It has a calculated hardness of 5.5 GPa in the $c$-axis [12].

All of the $W$ ferrites have uniaxial anisotropy, except $\text{Co}_2\text{W}$ ferrite ($\text{BaCo}_2\text{Fe}_{16}\text{O}_{27}$) [7], which has a molecular mass of 1581 g and a density of 5.31 g cm$^{-3}$ [8]. This has a cone of easy magnetisation at an angle of 70° to the $c$-axis from 0° to 180°, at which point this anisotropy rotates towards the $c$-axis with increasing temperature until it becomes uniaxial at 280 °C, and the magnetisation remains in the $c$-axis with a further rise in temperature [17].

2.3. The $X$ ferrites

The $X$ ferrites were first reported in 1952 as a mixed phase with $M$ or $W$ ferrite, and have the chemical formula $\text{Ba}_2\text{Me}_2\text{Fe}_{28}\text{O}_{46}$, where Me is a divalent first row transition metal or some other divalent cation. The first reported $X$ ferrite was $\text{Fe}_2\text{X}$, in which Me = $\text{Fe}^{2+}$ [18], and this was also found to have a uniaxial magnetic anisotropy along the $c$-axis and density of 5.29 g cm$^{-3}$ [8]. All the $X$ ferrites have this uniaxial anisotropy at room temperature, except for $\text{Co}_2\text{X}$ (molecular mass = 2688 g), which has a cone of magnetisation at an angle of 74° to the $c$-axis [19]. Like the $W$ ferrite it resembles, this cone changes to adopt an orientation parallel to the $c$-axis at a higher temperature, in this case 143 °C [20].

2.4. The $Y$ ferrites

The $Y$ ferrites were the first ferroxplana ferrites to be discovered, and it is now known that nearly all $Y$ ferrites have a preferred plane of magnetisation perpendicular to the $c$-axis at room temperature [7]. The formula of the $Y$ ferrites is $\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$, where Me is a small divalent cation, and the first two to be made were $\text{Zn}_2\text{Y}$ and $\text{Co}_2\text{Y}$. The molecular mass of $\text{Co}_2\text{Y}$ is 1410 g, and it has a density of 5.40 g cm$^{-3}$ [8].

$\text{Co}_2\text{Y}$ has a planar magnetic anisotropy at room temperature, but this changes to a cone of magnetisation below −58 °C. From this temperature to the Curie point the anisotropy remains in the preferred plane [7]. $\text{Cu}_2\text{Y}$ is the only $Y$ ferrite that has been found to have a preferred uniaxial direction of magnetisation [21].

2.5. The $Z$ ferrites

The $Z$ ferrites have the composition $\text{Ba}_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}$, and they were discovered at the same time as the ferroxplana $Y$ ferrites [7]. $\text{Co}_2\text{Z}$ has a molecular mass of 2522 g and a maximum density of 5.35 g cm$^{-3}$ [8]. The $Z$ ferrites all have a uniaxial anisotropy parallel to the $c$-axis, except for $\text{Co}_2\text{Z}$, which is planar at room temperature but has a complex magnetic anisotropy, with at least four different anisotropic states.

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<table>
<thead>
<tr>
<th>$\delta$</th>
<th>$T_m$</th>
<th>$x_a$</th>
<th>$x_c$</th>
<th>$x_v$</th>
<th>$a$</th>
<th>$c$</th>
<th>$V$</th>
<th>$T_c$</th>
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<td>SrM</td>
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<td>1692</td>
<td>8.62</td>
<td>16.08</td>
<td>33.50</td>
<td>5.8844</td>
<td>23.0632</td>
<td>691.6</td>
</tr>
<tr>
<td>BaM</td>
<td>5.295</td>
<td>1611</td>
<td>10.74</td>
<td>16.29</td>
<td>38.16</td>
<td>5.8876</td>
<td>23.1885</td>
<td>696.2</td>
</tr>
<tr>
<td>PbM</td>
<td>5.708</td>
<td>1538</td>
<td>10.80</td>
<td>18.34</td>
<td>40.46</td>
<td>5.8941</td>
<td>23.0984</td>
<td>694.9</td>
</tr>
</tbody>
</table>
2.6. The U ferrites

The U ferrites, $\text{Ba}_4\text{Me}_2\text{Fe}_{36}\text{O}_{60}$, although identified at the same time as the other hexagonal ferrites mentioned here, were not characterised much either structurally or magnetically until recently. The densities of $\text{Co}_2\text{U}$ and $\text{Zn}_2\text{U}$ have been calculated as 5.44 and 5.31 g cm$^{-3}$ [8,22]. They all have uniaxial anisotropy except $\text{Co}_2\text{U}$, which has planar anisotropy at room temperature [23], and a molecular mass of 3622 g.

2.7. Other hexagonal ferrites

Over 70 distinctive members of the hexagonal ferrites family have been discovered, related to either the W or Z ferrites. Most of these are extremely large and complex compounds, and the largest so far discovered has the formula $\text{Ba}_{70}\text{Me}_{86}\text{Fe}_{444}\text{O}_{802}$ and a molecular mass of 52 450 g (52.45 kg) [24].

3. The structure of the hexagonal ferrites

All of the hexagonal ferrites have closely related, highly complex crystal structures [18], which can be interpreted in various ways as summarised in Table 3. At a simple level, they can all be seen as molecular combinations of the three ferrite compounds S (spinel, $\text{MeFe}_2\text{O}_4$), M ($\text{BaFe}_{12}\text{O}_{19}$) and Y ($\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$). W ferrite, $\text{Ba}_2\text{Me}_2\text{Fe}_{16}\text{O}_{27}$, can be considered as $\text{M} + 2\text{S}$, X ferrite ($\text{Ba}_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}$) = $\text{M} + \text{Y}$, and U ferrite ($\text{Ba}_4\text{Me}_2\text{Fe}_{36}\text{O}_{60}$) = $\text{Z} + \text{M} = 2\text{M} + \text{Y}$. HRTEM images of the stacking of these layers have been published by Sudakar et al. [25]. The other larger hexagonal ferrites are similarly composed. The $\text{Ba}^{2+}$ ion is large, as is the $\text{O}^{2-}$ ion, and the barium always replaces an oxygen atom somewhere in the oxygen lattice. As the barium ion is slightly smaller than the oxygen ion, it distorts the lattice in its immediate vicinity. The barium ion can be substituted by another divalent metal provided it is of sufficient size, such as strontium or lead, to maintain the structure without too much distortion. $\text{Fe}^{3+}$ and $\text{Me}^{2+}$ are much smaller ions and insert themselves in interstices between the oxygen positions, and as in inverse spinels, both divalent and trivalent ions inhabit both octahedral and tetrahedral sites in the oxygen framework, as well as the trigonal bipyramidal site that exists in hexaferrites that contain the R block.

To describe a hexagonal crystal four Miller indices $h$, $j$, $k$ and $l$ are needed. The principal axis is in the (0001) direction along the length of the crystal, and the three other axes are across the basal (0001) plane of the hexagonal polyhedron at angles of 120° to each other. The principal axis is named the c-axis and its length is the c lattice parameter. In the ferrites the three axes of the hexagonal plane are all equal, and so only one other parameter, a, is required to describe a regular hexagonal crystal, which is the length of one of the sides of this plane. Therefore, only two lattice parameters, c and a, are needed to give the dimensions of the crystal.

Table 3

Comparison of various descriptions of the molecular units of hexagonal ferrites. * = 180° rotation of that block around the c-axis.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Molecular formula</th>
<th>Molecular units</th>
<th>Spinel plates and hexagonal layers</th>
<th>Hexaferrite blocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>$\text{CoFe}_2\text{O}_4$</td>
<td>S</td>
<td>$S_1$</td>
<td>1/2 S</td>
</tr>
<tr>
<td>M</td>
<td>$\text{BaFe}<em>{12}\text{O}</em>{19}$</td>
<td>M</td>
<td>$M_5 = B_1S_4$</td>
<td>SR</td>
</tr>
<tr>
<td>W</td>
<td>$\text{BaCo}<em>2\text{Fe}</em>{16}\text{O}_{27}$</td>
<td>$M + 2S$</td>
<td>$W_5 = M_5S_2 = B_1S_4$</td>
<td>SSR</td>
</tr>
<tr>
<td>X</td>
<td>$\text{Ba}<em>3\text{Co}<em>2\text{Fe}</em>{24}\text{O}</em>{46}$</td>
<td>2 $M + 2S$</td>
<td>$X_{12} = \text{M}_5S_2 \text{M}_5 = B_1S_4B_1S_6$</td>
<td>SRS, S'R'R'</td>
</tr>
<tr>
<td>Y</td>
<td>$\text{Ba}<em>2\text{Co}<em>2\text{Fe}</em>{12}\text{O}</em>{22}$</td>
<td>Y</td>
<td>$Y_6 = B_3S_4$</td>
<td>ST</td>
</tr>
<tr>
<td>Z</td>
<td>$\text{Ba}<em>3\text{Co}<em>2\text{Fe}</em>{24}\text{O}</em>{41}$</td>
<td>$Y + M$</td>
<td>$Z_{11} = Y_6M_5 = B_3S_4B_4S_4$</td>
<td>S1SR</td>
</tr>
<tr>
<td>U</td>
<td>$\text{Ba}<em>4\text{Co}<em>2\text{Fe}</em>{36}\text{O}</em>{60}$</td>
<td>$Y + 2M$</td>
<td>$U_{10} = M_2Y_6 \text{M}_5 = B_3S_4B_2S_4B_1S_4$</td>
<td>SRS, R'S'T</td>
</tr>
</tbody>
</table>
3.1. The spinel-based model

The structures can also be thought of as plates of cubic close packed oxygens with smaller metal ions in octahedral and tetrahedral interstices, in the same arrangement as the spinel structure. The spinel is a close-packed cubic structure, in which the positions of the layers of four oxygen atoms repeat every three vertical layers to form an ABCABC lattice, these layers being approximately 2.30 Å apart. In the spinel structure, the interstices between these cubic layers are alternatively filled with three octahedral sites and one octahedral and two tetrahedral sites per four oxygen atoms (Fig. 4). The spinel layers form plates either four or six oxygen layers thick, and between the outer two layers at both ends of the plates only octahedral sites are occupied by the metal atoms. The W structure contains only six-layer plates (S₆), the X structure consists of alternating six- and four-layer plates (S₆ and S₄) and M, Y, Z and U of only S₄ plates [18].

These spinel plates are joined together by two possible barium containing layers, which both have a hexagonal close-packed structure which repeats every two vertical layers forming an ABAB lattice. The B₁ layer is a single hexagonal close-packed layer with 3-fold symmetry between two spinel plates, in which one of the four oxygen atoms is replaced by a barium atom, with the remaining oxygen atoms grouped in two sets of triangles. The metal atoms are in plane in the centre of one triangle and out of plane at about half the layer distance above and below the centres of the other sets of triangles (Fig. 5). These layers hold spinel plates so they always contain a mirror plane in the B₁ layer, giving rise to a sequence of hexagonal close packed layers. The B₁ layer appears in M, W and Z ferrites, where the mirror plane reflects the entire structure, and in X ferrite where it only reflects a limited number of adjacent layers [18].

The B₂ layer consists of two hexagonal close-packed layers between two spinel plates, in which one of the four oxygen atoms in each layer is replaced by a barium atom, giving two barium atoms in the B₂ layer. The barium atom in one layer is in contact with the three oxygen atoms of the other layer, and the octahedral sites between the oxygen atoms contain the small metal ions. There are other metal

![Fig. 4. Cross sectional view [8] of the spinel structure, showing the S block, Me₂Fe₄O₈ (two units cells of spinel). The three S blocks indicated here equate to six-layer plates (S₆). The arrows represent the orientation of the magnetic moments of the cations, and the vertical lines are axes of threefold symmetry.](www.iran-mavad.com)
ions sites at one layer distance above and below, and there are more just out of the plane opposite each barium atom (Fig. 5). These B$_2$ layers form a hexagonal close packed array with the adjacent spinel layers only. They occur in Y ferrite, which contains only B$_2$ layers, and Z ferrite, in which they alternate with the B$_1$ layers [18].

This rather confusing representation describes the structures of the hexagonal ferrites in terms of mostly cubic plates separated by hexagonal layers. The relationships between the structures are better demonstrated by combining the S and B layers into three distinct units which can be used to make any of the hexagonal ferrites, S$_2$ = two spinel layers, M$_5$ = a B$_1$ layer sandwiched between four spinel layers (M ferrite), and Y$_6$ = two B$_2$ layers sandwiched between four spinel layers (Y ferrite), as depicted in Fig. 5.

A superior way to describe the hexagonal structures is as being made out of three distinct blocks, related to the units above, which better relate to their unit cells and chemical compositions [8,26]. The blocks also have discrete magnetic characteristics that can be summed to give the saturation magnetisations of the whole ferrite, and these are discussed in chapter five. The structures of the blocks and each ferrite are discussed separately in the following sections.
3.2. The S, R and T blocks

The S block consists of two spinel units and therefore has the unit formula \( \text{Me}_2\text{Fe}_4\text{O}_8 \), where \( \text{Me} = \) a divalent metal ion, and is equivalent to the \( \text{S}_2 \) unit (Fig. 6). Therefore, each S block consists of two layers of four oxygen atoms with three metal atoms between each layer, in four octahedral sites where the cation is surrounded by six oxygen anions and two tetrahedral sites where four oxygen anions surround the cation.

The R block consists of three hexagonally packed layers of four oxygen atoms each, but one of the oxygen atoms in the centre layer is replaced by a similarly sized barium atom to give the unit formula \( \text{BaFe}_6\text{O}_{11} \). This is equivalent to the \( \text{M}_5 \) unit with the top and bottom layers removed. The single barium atom in the block creates an asymmetry in some of the cation sites, resulting in five octahedral sites, no tetrahedral sites as they are pushed into octahedral sites by the bulky barium atom, and a five-coordinate trigonal bipyramidal site in which the cation is surrounded by five oxygen anions, a unique position only found in the R block (Fig. 6).

The T block is made of four oxygen layers, with a barium atom replacing an oxygen atom in the middle two layers, to give the unit formula \( \text{Ba}_2\text{Fe}_8\text{O}_{14} \) (Fig. 6), and again this is the \( \text{Y}_6 \) unit with the top and bottom layers removed. Because there are two large barium atoms opposite each other in

---

**Table 4**

Comparison of various descriptions of the unit cells of hexagonal ferrites. \( \ast = 180^\circ \) rotation of that block around the c-axis.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Unit cell</th>
<th>Spinel plates and hexagonal layers</th>
<th>Hexaferrite blocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>2M</td>
<td>( 2\text{M}_2 = \text{B}_1\text{S}_3\text{B}_1\text{S}_4 )</td>
<td>SRS' R'</td>
</tr>
<tr>
<td>W</td>
<td>2W</td>
<td>( 2\text{W}_7 = 2(\text{M}_2\text{S}_2) = \text{B}_1\text{S}_3\text{B}_5 )</td>
<td>SSRS' S'R'</td>
</tr>
<tr>
<td>X</td>
<td>3X</td>
<td>( 3\text{X}_{12} = 3(\text{M}_3\text{S}_5\text{M}_3) = \text{B}_1\text{S}_4\text{B}_1\text{S}_1\text{S}_6\text{B}_1\text{S}_1\text{S}_6 )</td>
<td>3(5RS'S'R')</td>
</tr>
<tr>
<td>Y</td>
<td>3Y</td>
<td>( 3\text{Y}_5 = \text{B}_5\text{S}_6\text{B}_2\text{S}_2\text{S}_4 )</td>
<td>3(ST)</td>
</tr>
<tr>
<td>Z</td>
<td>2Z</td>
<td>( 2\text{Z}_{11} = 2(\text{Y}_6\text{M}_3) = \text{B}_2\text{S}_2\text{B}_2\text{S}_2\text{B}_1\text{S}_4 )</td>
<td>STSR'S'T'S'R'</td>
</tr>
<tr>
<td>U</td>
<td>U</td>
<td>( \text{U}_{16} = (\text{M}_5\text{Y}_6\text{M}_3) = \text{B}_5\text{S}_2\text{B}_2\text{B}_2\text{B}_1\text{S}_4 )</td>
<td>SRS'R'S'T'</td>
</tr>
</tbody>
</table>

---

**Fig. 6.** Perspective view [26], space filling view [27] and ball-and-stick view [27] of the S, R and T blocks.
Fig. 7. (a) Cross section view of the M ferrite (BaFe$_{12}$O$_{19}$) structure in which the vertical lines are axes of threefold symmetry [8]. (b) [26] and (c) [28] Perspective views of the M unit cell. (d) The polyhedra of the M unit cell [29]. (e) The RSR'S' stacking sequence [30]. The arrows indicate the orientations of the magnetic moments of the cations relative to the $c$-axis, $\alpha = 180^\circ$ rotation of the block around the $c$-axis, $m$ = mirror plane.
Fig. 8. (a) Cross section view of the W ferrite structure (BaMe$_2$Fe$_{16}$O$_{27}$) in which the vertical lines are axes of threefold symmetry [8]. The arrows indicate the orientations of the magnetic moments of the cations relative to the c-axis, $\varphi = 180^\circ$ rotation of the block around the c-axis, m = mirror plane. In Co$_2$W the moments will be in the preferred cone of magnetisation, at an angle to the c-axis at room temperature. (b) Perspective view of the W structure [26]. (c) W ferrite polyhedra (Me1–7 represent the seven different polyhedra in SrZnCoW) [31]. (d) 3-D model of a W ferrite unit cell.
adjacent layers, both the barium and cations which would have been in the five coordinate sites are pushed away in opposite directions. This reduces the five-coordinate trigonal bipyramidal sites to four-coordinate tetrahedral sites, resulting in two tetrahedral and six octahedral sites.

The actual unit cells of most hexagonal ferrites consist of multiples of the molecular ferrite, two molecular units for M, W and Z ferrite, and three molecular units for X and Y ferrite, but only one molecular unit for U ferrite. Due to the complex nature and large size of the unit cells, individual crystals of these ferrites can be very large. The various depictions of the unit cell are summarised in Table 4.

3.3. The M structure

The molecular unit of M ferrite is made of one S and one R block, with an overlap of hexagonally and cubically packed layers. The basal plane containing the barium atom is a mirror plane, and the two S blocks above and below the R block are therefore 180° rotations around the c-axis of each other. A mirror R block, R*, is then required to continue the structure, and it is for this reason that the unit cell requires two molecular M units, giving the unit cell formula SRS'R*, where * = a rotation of the block through 180° around the c-axis (Fig. 7a) The lattice parameters of BaM are 23.17 Å for the c-axis length and 5.89 Å for a, the width of the basal plane, and this a-parameter is constant for all the barium hexagonal ferrites [18]. The ratio of height to width is 3.94, so BaM has a large crystalline anisotropy, which becomes even higher for the other hexagonal ferrites. Perspective views of the structure are also shown in Fig. 7b and c, while the polyhedra of the M structure, including the bipyramidal site of the R block, are shown in Fig. 7d. Fig. 7e depicts the stacking of the R and S blocks in the M structure.

SrM has smaller lattice constants due to the smaller size of the Sr^2+ ion, giving the parameters c = 23.03 Å and a = 5.86 Å. Otherwise it has the same structure and unit cell ordering as BaM [14]. The Pb^2+ ion is also smaller than Ba^2+, and the lattice parameters for PbM are c = 23.02 Å, a = 5.88 Å [3].

3.4. The W structure

The molecular unit of W ferrite is composed of two S blocks and one R block, so it is similar to the M structure but not identical. There are now two S blocks above and below the R block, but again there is
a mirror plane in the R block and the unit cell consists of two molecular W units to give SSRS’SR’. The cell length of Fe₂W is 32.84 Å, it is a member of the space group P6₃/mmc, and the structure is shown in Fig. 8 [18].

3.5. The X structure

The X structure is very similar to that of W, being composed of one M and one W molecular units (Fig. 9), to give the structure SRS’SR’, with the blocks of the W section rotated through 180° relative to the M section. The unit cell is constructed from three identical units to give the crystal structure 3(SRS’SR’), c = 84.11 Å, and it is a member of the R₃m space group [18].

3.6. The Y structure

The molecular unit of Y ferrite is one S and one T unit, with a total of six layers, the unit cell consists of three of these units, with the length of the c-axis being 43.56 Å, and is a member of the space group R₃m [18]. The T block does not have a mirror plane, and therefore a series of three T blocks is required to accommodate the overlap of hexagonal and cubic close packed layers, with the relative positions of the barium atoms repeating every three T blocks. This gives the unit cell formula as simply 3(ST), and the structure is shown in Fig. 10.

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Fig. 10. Left: Cross section view of the Y ferrite (Ba₂Me₂Fe₁₂O₂₂) structure in which the vertical lines are axes of threefold symmetry [8]. The arrows indicate the orientations of the magnetic moments of the cations relative to the c-axis. Right: Perspective view of the Y structure [26].
Fig. 11. (a) Cross section view of the Z ferrite ($\text{Ba}_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}$) structure in which the vertical lines are axes of threefold symmetry [8]. The arrows indicate the orientations of the magnetic moments of the cations relative to the $c$-axis, $m = 180^\circ$ rotation of the block around the $c$-axis, $m = $ mirror plane. In Co$_2$Z the moments will be in the preferred plane of magnetisation, perpendicular to the $c$-axis at room temperature. Right: (b) [26] and (c) [32] Perspective views of the Z structure, also showing the ten Wyckoff positions for cations, Me1–Me10.
3.7. The Z structure

The Z unit is composed of Y + M, and therefore consists of ST + SR, with a mirror plane in the R block and a repeat distance of 11 oxygen layers. Therefore, two molecular units are required to form a single unit cell of Z ferrite, one rotated 180° around the c-axis relative to the other, to give STSRS'T'S'R", with a c axis length of 52.30 Å (Fig. 11), and it is a member of the space group P6₃/mmc [18]. Perspective views of the unit cell are also shown in Fig. 11.

3.8. The U structure

The U ferrite structure has been found to consist of the molecular units Z + M, or M + Y + M, to give the block structure SRS'R'S'T (Fig. 12). Unusually the unit cell was originally stated to consist of only one molecular unit, where c = 38.16 Å [24], in which the R and S blocks of the Z section are rotated through 180° relative to the M section. These days it is more usually stated as consisting of three molecular units, with a = 5.88 and c = 113 Å [33]. HRTEM images have shown clearly the MMY stacking sequence of U ferrite, as well as stacking faults where the crystal structure is interrupted by incorporation of additional Y blocks (Fig. 13) [33]. The repeating R, S and T blocks of Sr₄Co₂U can clearly been seen in HAADF-STEM in Fig. 12, as the Sr²⁺ ion is smaller than Ba²⁺, the lattice parameters for Sr₄Co₂U are a = 5.86 Å and c = 112.3 Å, with the R3m space group [34].

3.9. The structures of higher hexagonal ferrites

TEM evidence of the complex stacking of these various M and Y layers has been shown by Sudakar et al. [25] for BaM, Ni₂Y, Ni₂W, Ni₂Z, Ni₂X and Ni₂U (Fig. 14), and Lisjak et al. for Co₃U Zn₂U and Ni₂U

Fig. 12. Left: Cross section view of the U ferrite (Ba₄M₂Fe₃₆O₆₀) structure in which the vertical lines are axes of threefold symmetry, and the arrows indicate the orientations of the magnetic moments of the cations relative to the c-axis [26]. (In this case, one molecular unit is shown). Right: High-angle annular dark field scanning TEM (HAADF-STEM) image of Sr₄Co₂U along the [110] direction, with a diagram of the corresponding structure. In HAADF-STEM the heavy Sr atoms show as bright spots [34].
Sudakar et al. also measured the height of the M, Y and W blocks to be 1.16, 1.45 and 1.68 nm, respectively, along the c-axis [25]. Both investigations found evidence of stacking faults in the more complex Z, X and U ferrites at higher temperatures up to 1350°C. Despite this, the structures of at least 61 different hexagonal ferrites have so far been established, including the ferrites mentioned above. These are divided into two groups, and in the higher hexagonal ferrites the molecular unit and unit cell are equivalent, as with Co₂U. The M-S series has five members, basic M ferrite without an S unit, and four others of the formula MₙS, where n = 1, 2, 4 and 6. When n = 1 W ferrite is formed and n = 2 is X ferrite. The end member of this group, M₆S, has a molecular formula of Ba₆Me₂Fe₇₆O₁₂₂ and a unit cell length of 223.4 Å. The other series is MₙYₚ, in which n = 1, 2, 4, 6, or 8 and p = up to 33, and there are 56 members of this group including Y (n = 0, p = 1), Z (n = p = 1) and U (n = 2, p = 1). The highest ferrite so far reported is the enormous Ba₇₀Me₈₆Fe₄₄₄O₈₀₂ with the unit formula M₄Y₁₃, in which the units are in the sequence MY₉MY₁₀MY₇MY₁₀, and this has the largest inorganic unit cell ever seen at c = 1577 Å (0.16 μm!). The smaller Ba₆₂Me₅₄Fe₄₂₀O₇₄₆ is the most structurally complex ferrite, with over 400,000 possible permutations for the sequence of the M₈Y₂₇ units. They occur in the sequence MMMY₆MY₇MYMY₆MY₈ and c = 1455 Å [24].

### 3.10. Electrical conductivity of ferrites

Although the hexagonal ferrites are good electrical resistors, if the bivalent ferrous (Fe²⁺) ion is associated with the ferric (Fe³⁺) ion, even in small amounts, it lowers the resistance greatly as an interchange (“hopping”) of electrons can occur very readily, generating a current [35]. This is why magnetite is such a good electrical conductor for an oxide. There are two possible conduction mechanisms, n-type electron conduction and p-type hole conduction. In high resistance materials, if one cation is replaced by another that seeks a lower valency level then p-type conduction occurs, if the cation prefers a higher valency then it results in n-type. In ferrites excess iron (or oxygen deficiency...
during sintering at high temperatures) promotes Fe$^{2+}$ formation and n-type conduction results, but an iron deficiency results in p-type conduction, which is very poor in ferrites [36]. Therefore, an excess of iron should be avoided if the material is to have any electrical applications. Unfortunately, the high sintering temperatures needed to promote a dense product also increase the proportion of Fe$^{2+}$ in the ferrite, although an addition of manganese or cobalt in amounts as small as 0.02% lowers resistance by several orders of magnitude [37]. Furthermore, in polycrystalline ceramic ferrites, low resistance grains are separated by highly resistive grain boundaries, creating an interfacial polarisation that can lead to conductivity – this will be reduced in larger grained ferrites. It has been claimed that in cobalt containing ferrites, the tendency of Fe$^{3+}$ → Fe$^{2+}$ will be reduced by the reaction Fe$^{2+}$ + Co$^{3+}$ → Fe$^{3+}$ + Co$^{2+}$, and that other stable multivalent ions such as Mn will have a similar effect. It is thought that Mn$^{3+}$ will increase resistivity to a greater extent than Co$^{3+}$, as it forms a localised stable pair Mn$^{3+}$–Fe$^{2+}$, preventing electrons from leaving the Fe$^{2+}$ for other ferric ions [38].
Conduction mechanisms in W ferrites have been more studied than many due to their electrical applications, and recent modelling has suggested that Fe$_2$W is more conductive than Co$_2$W because it contains mixed valence ions (Fe$^{3+}$ and Fe$^{2+}$) in the 6g sites at the interface between the two S layers, resulting in an electrically conductive layer. In Co$_2$W this 6g site is occupied only by Co$^{2+}$ ions, greatly lowering the electron carrier density. This conduction is also anisotropic, with a much greater resistivity along the c-axis, perpendicular to this conductive layer [39]. RT AC and DC conductivities have been measured for Co$_2$W as being $3 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$ and $5 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$, respectively, at low frequencies (~1 kHz), and they increase with increasing frequency or temperature [40]. Substituting Co with Ni$^{2+}$ or Cu$^{2+}$ increases conductivity by several orders of magnitude. BaM has a reasonably high RT conductivity of $2 \times 10^{-4}$ $\Omega^{-1}$ cm$^{-1}$, but this can be reduced greatly as (Co$^{2+}$/Ti$^{4+}$) is substituted for Fe$^{3+}$, decreasing by five orders of magnitude to $7 \times 10^{-9}$ $\Omega^{-1}$ cm$^{-1}$ for BaCo$_{0.5}$Ti$_{0.5}$Fe$_{11}$O$_{19}$ [41].

3.11. Iron oxides

The common forms of iron(III) oxide are haematite ($\alpha$-Fe$_2$O$_3$) and maghemite ($\gamma$-Fe$_2$O$_3$). Haematite is a hexagonal crystal based on hexagonal close packing of O$^{2-}$ with 2/3 of the interstices filled with Fe$^{3+}$, each cation being surrounded by 6 O$^{2-}$ ions, and it can act as a nucleation site for the growth of other hexagonal species such as $\alpha$-FeOOH or $\alpha$-Al$_2$O$_3$ [42]. The similar oxyhydroxide goethite ($\alpha$-FeOOH) has the Fe$^{3+}$ ion occupying 1/2 of the sites, with each cation surrounded by 3 O$^{2-}$ and 3 OH$^{-}$ ions.

Maghemite resembles the cubic magnetite (Fe$_3$O$_4$), which is an inverse spinel with Fe$^{3+}$ ions occupying some of the tetrahedral sites normally only inhabited by M$^{2+}$ ions, but in maghemite cation vacancies compensate for the oxidation state of the missing Fe$^{2+}$ ions. This leaves the Fe$^{3+}$ randomly distributed over a mixture of tetrahedral and octahedral sites with only octahedral vacancies [43]. The compound could better be thought of as Fe$_{2.67}$$\square_{0.33}$O$_4$, where $\square$ = a vacancy, and it is really a solid solution with a variable cell parameter [44]. In the iron oxides the Fe$^{3+}$ ion is always in the high spin d$^5$ state with all electrons unpaired, and has no preference for octahedral or tetrahedral sites [42].

4. Synthesis methods for hexagonal ferrites

The formation of the hexagonal ferrites is an extremely complicated process, and the mechanisms involved are not fully understood despite having been investigated by many researchers for over 50 years [21,45–48]. If a non-stoichiometric mixture of BaO·Fe$_2$O$_3$·CoO is heated the following products generally form and decompose in this order:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Major products</th>
<th>Minor products</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 °C</td>
<td>$\alpha$-Fe$_2$O$_3$, Co$_3$O$_4$, BaO</td>
<td>CoFe$_2$O$_4$, BaFe$_2$O$_4$</td>
</tr>
<tr>
<td>600 °C</td>
<td>$\alpha$-Fe$_2$O$_3$, Co$_3$O$_4$, BaO</td>
<td>BaM, BaO</td>
</tr>
<tr>
<td>700 °C</td>
<td>$\alpha$-Fe$_2$O$_3$, CoFe$_2$O$_4$, BaFe$_2$O$_4$</td>
<td>$\alpha$-Fe$_2$O$_3$, CoFe$_2$O$_4$</td>
</tr>
<tr>
<td>800 °C</td>
<td>BaM, BaFe$_2$O$_4$</td>
<td>BaFe$_2$O$_4$, CoFe$_2$O$_4$</td>
</tr>
<tr>
<td>900 °C</td>
<td>BaM, Y</td>
<td>BaFe$_2$O$_4$, CoFe$_2$O$_4$</td>
</tr>
<tr>
<td>1000 °C</td>
<td>BaM, Y</td>
<td>BaFe$_2$O$_4$, CoFe$_2$O$_4$</td>
</tr>
<tr>
<td>1100 °C</td>
<td>Y, BaM</td>
<td>BaFe$_2$O$_4$</td>
</tr>
<tr>
<td>1200 °C</td>
<td>Z, Y, BaM</td>
<td>W</td>
</tr>
<tr>
<td>1300 °C</td>
<td>Z</td>
<td>Y, W</td>
</tr>
<tr>
<td>1400 °C</td>
<td>W, Z</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen (Fig. 16), the different hexagonal phases all overlap, and except for the M ferrites they all need high temperatures of at least 1000 °C to become the major phase. This makes it extremely hard to obtain single phase specimens of some of these ferrites, and their particle size tends to be large due to the high temperatures required. At temperatures over 1200 °C an exaggerated grown pattern is seen, in which some particles grow to a much greater extent and at a greater rate than their neighbours, even in a single phase material. This morphology, containing a wide spread
of particle diameters ranging up to many tens or even hundreds of μm, is named discontinuous grain growth (DGG), and individual hexagonal grains up to 1 mm in diameter can occur. The solid state reactions and synthesis methods of specific ferrites are examined in more depth in Section 4.

4.1. Standard ceramic techniques

Standard ceramic techniques used to prepare the hexagonal ferrites involve heating a mixture of oxide and barium carbonate powders to produce the desired phase. The ceramic product then usually has to be milled and powdered to produce a finer material, and then sintered to increase density. The high temperatures and long firing times required usually result in a coarse grain product, with average grain sizes between 1 and 10 μm for the M ferrites, and up to 50 μm for the higher hexagonal phases, such as Y, Z and W. However, if the starting materials are intimately mixed at the atomic or ionic level before reaction, crystallisation occurs at lower temperature resulting in smaller particles and lower sintering temperatures, and the fully densified material can often be produced in one step. This can be achieved by high energy mechanochemical milling, typically in a high energy planetary ball mill. Not only does this finely disperse powders which can be nanosized after long milling, but the actual synthesis of compounds can occur through chemical assembly with greatly reduced activation energies due to the small particle size and energy from the milling process. The nature of hexaferrites being assembled from pre-existing crystalline building blocks via topotactic reactions many make them ideal for this type of synthesis, especially the more complex compounds. Converting the ferrites into an ultrafine dispersed solid-state of nanoagglomerates or nanoclusters allows nanoparticles to participate in the thermal motion and provides for the possibility of their self-assembly into superstructures by eventually finding the thermodynamic optimum.” [49]. However, there are many other methods to prepare hexaferrites, and most of those discussed in the following sections are based on precipitation of a ferrite precursor at some point, and achieve hexaferrite synthesis to varying degrees of success.

4.2. Coprecipitation

The chemical coprecipitation of salts with a base, resulting in a precipitate containing all the components mixed at an ionic level, has been used to produce ferrites since the early 1960s [50,51]. It has often been found that an iron deficient non-stoichiometric mixture must be used, for example with an Fe:Ba ratio of 10–11 for BaM, instead of the correct ratio of 12 [52]. SrM from coprecipitates needs an even lower Fe:Ba ratio of less than 9 to give pure M [53]. Using this process BaM can be formed at temperatures between 750 and 900 °C with a submicron grain size, and the density of the product can be increased if it is washed by centrifuge as opposed to decantation [54].

To improve homogeneity, a wet chemical process was developed in which an aqueous solution of metal salts was precipitated with a strong base, and the resultant hydroxide oxidised by bubbling air through the suspension to give a homogenous fine grained ferrite product [55]. In more recent work a non-stoichiometric solution of iron(II) salts and barium salts are coprecipitated with NaOH at pH 14, and the resultant hydroxides are oxidised with hydrogen peroxide (H₂O₂) and then washed to pH 7. The dried hydroxides are then heated, producing pure BaM at the very low temperature of 600 °C and with a grain size below 0.1 μm [56]. Sodium hypochlorite (NaClO) has also been employed for a similar purpose to produce BaM [56]. Co₂Z has been made from the coprecipitation of very dilute solutions of barium and cobalt chlorides and iron nitrate, the precipitates being reacted together with acetic acid and an organic stabiliser, filtered, and then processed by normal ceramic routes to form Co₂Z [57].

4.3. Salt-melt method

In this technique a solution of metal chlorides is coprecipitated by NaOH, Na₂CO₃ or NaHCO₃ and then the salts NaCl and/or KCl are added to this mixture, which is then dried and heated to a flux between 600 and 1100 °C to give a mixture of the ferrite material and the alkaline metal salts on cooling [58]. The original process was less sophisticated, involving just a mixture of the standard ceramic precursors BaCO₃ and Fe₂O₃ heated in a flux of a NaCl–KCl mixture [59], but the coprecipitation stage
results in a superior product. The sodium and potassium salts can be easily removed from the ferrite by washing with water or dilute acid, although there is inevitably some contamination of the ferrite product with the alkaline metals. BaM with good magnetic properties has been made by this process in a non-stoichiometric mixture with an Fe:Ba ratio of 10, and the submicron grain size and magnetic properties can be varied by changing the compositions of the fluxing components [60]. The highly insoluble sulphates are the cheapest and most abundant minerals of barium and strontium, and a salt-melt consisting of these sulphates, Fe$_2$O$_3$ waste from steel pickling and Na$_2$CO$_3$ with the Fe:Ba ratio of 11 has been used to make pure SrM and BaM over 860 °C [61].

A variation on this method is melt-flux precipitation, in which less fluxing material is added, so that instead of a true liquid phase system forming there are only microregions of slightly melted salt in which the crystallisation occurs. This has been employed to make BaCoTiM from mixtures of $\gamma$-Fe$_2$O$_3$, BaCO$_3$, CoCO$_3$, TiO$_2$ and the fluxing agents 7BaCl$_2$. When the melt-flux was heated radiothermally by an electron beam instead of normal thermal heating, the pure ferrite was formed at a lower temperature and with a grain size one third of the size at under 100 nm [63].

4.4. Ion exchange

The compound KFe$_{11}$O$_{17}$, or $\beta$-ferrite, is isomorphous with the M ferrites, but has no magnetic moment [18]. A cobalt doped BaM with the formula BaFe$_{11.5}$Co$_{0.5}$O$_{19}$ was made from the ion exchange of Ba$^{2+}$ for K$^+$ in the compound $\beta$'-ferrite, KFe$_{10.5}$Co$_{0.5}$O$_{17}$, which was first synthesised from a stoichiometric mixture of metal chlorides heated to 700 °C. This compound was then added to a salt-melt of BaCl$_2$ and KCl at 750 °C for 24 h, at the end of which a total substitution of Ba$^{2+}$ for K$^+$ had occurred in 75% of the material, the rest remaining as $\beta$'-ferrite. After annealing at 900 °C the grain size of the M phase was 200 nm, and despite being 25% impure the magnetic properties were acceptable as the $\beta$'-ferrite is non-magnetic [64]. When the same synthesis was attempted in an aqueous solution of nitrates instead of a salt-melt only a partially substituted M compound resulted, containing both Ba$^{2+}$ and K$^+$ ions, which had poor magnetic properties [65]. SrM single crystals have also been produced from the ion exchange of $\beta$'-ferrite single crystals [66].

4.5. Sol–gel

The sol–gel process mixes precursor particles, which can be inorganic or metallo-organic, on the colloidal scale, this mixing being retained when the material is condensed to a gel, and fine grained polycrystalline ferrites have been prepared by this method with a narrow size distribution. In aqueous sol–gel synthesis, an aqueous solution of metal salts is coprecipitated by a base, but instead of then drying and firing the precipitates are treated to form a colloidal sol, which can then be concentrated to a gel and subsequently fired to give the ferrite [67]. The sol must be very basic if it contains precipitated Ba(OH)$_2$ as this compound is only stable at a high pH, and such a sol cannot therefore be formed by acid digestion and peptisation. An organic coordinating agent such as ethylene glycol is often added to the hydroxide solution to produce a sol, which forms a gel structure upon evaporation of the water. When BaM was made from a sol–gel route involving the evaporation of glycol containing coprecipitated salts to give a homogenous gel, it was still found that a non-stoichiometric mixture was needed, and a ratio of Fe:Ba of 10.5 gave M ferrite at 900 °C/1 h with a grain size of only 200 nm [68]. Only the barium rich precursor yielded pure M without any $\alpha$-Fe$_2$O$_3$ as a second phase, but with a ratio of less than nine BaFe$_2$O$_4$ appeared as a secondary phase instead [69], indicating that there is only a narrow compositional window for the formation of BaM by this method. An acid sol was produced by dissolving precipitated and washed iron(III) hydroxide in a citric acid solution at 60 °C, to which BaCO$_3$ was added in the ratio Fe:Ba = 11.6, and evaporated to form a viscous residue which formed a gel at 170 °C. After prefiring to remove the organic components this produced single phase BaM at 750 °C which consisted of hexagonal crystals in a narrow diameter range of 90–110 nm, and subsequent annealing had little effect on the grain size [70].

Pullar et al. developed a novel aqueous sol–gel route for the preparation of a range of hexagonal ferrites from stoichiometric precursors, by adding barium, strontium and cobalt salts to an acid-peptised iron(III) hydroxide (FeOOH) sol. This was used to prepare BaM [71], SrM [72], Co$_2$Y [73],
Co$_2$W [74], Co$_2$Z [75], Co$_2$X [76] and Co$_2$U [76] ferrites, which were also then blow-spun to produce continuous fibres. Both halide and nitrate salts, and halide- and nitrate-stabilised sols, were investigated. Stability of a sol, and how concentrated it can be made, is important for subsequent processing, such as spin coating, thick films and fibre production. Both halide- and nitrate-stabilised undoped iron(III) sols were very stable, with sol particle sizes of 4.7 and 6.8 nm respectively and low polydispersity, but the sol stabilised by halide counterions was more stable, and it could be concentrated up to 35.5% Fe$^{3+}$ with only water as a solvent, while the nitrate based iron(III) sol had a maximum concentration of 23.5% Fe$^{3+}$ [77]. This was attributed to the fact that NO$_3^-$ counterions are known to elongate α-Fe$_2$O$_3$ particles to needles >100 nm, while Cl$^-$ counterions form smaller spherical ions, and a similar effect may be occurring in these amorphous FeOOH sols. Indeed, the upper limit of sol particle size produced a much larger “tail” of up to 31.5 nm for the volume average in the nitrate sol, as opposed to 20 nm for the halide sol [77], and a small number of larger particles is key in causing a sol to destabilise and precipitate upon concentration. It was found that the sols were also more stable when barium halide salts were added, as opposed to barium nitrate, due to the relatively low solubility in water of BaNO$_3$, and even if barium halide salts were added to a NO$_3^-$ stabilised iron(III) sol, it became unstable due to the formation of Ba(NO$_3$)$_2$. This problem was not observed when SrNO$_3$ was used, or when strontium halide salts were added to a nitrate-stabilised iron(III) sol, as SrNO$_3$ is much more soluble in water. The stoichiometric SrM precursor made from an NO$_3^-$ based sol was very stable with a monodisperse average sol particle size of only 8 nm which could be concentrated up to 17% Fe$^{3+}$, while the BaM precursor sol made from nitrates was polydisperse and much less stable, with an average sol particle size of 54 nm and an upper limit of 282 nm [77]. It was also found that the addition of a crown ether chelating ligand to the sol greatly increased the stability of all barium containing sols. Using a nitrate-free sol–gel system, with the addition of a cobalt halide salt as well, very stable stoichiometric sol precursors were made of all the hexagonal ferrites named above, with average sol particle sizes under 10 nm in all cases, and all of these converted to the single phase compared hexaferrites upon heating to between 700 °C (SrM) and 1200 °C (Co$_2$W and Co$_2$Z) [71–76]. It was found to be impossible to make any barium-containing sols using either any sulphate salts, or a SO$_4^{2-}$ or SO$_3^{2-}$ stabilised iron(III) sol, due to the almost total insolubility of barium sulphate.

In the synthesis of BaM from an organic sol–gel precursor, crystallisation occurs from 680 °C as the iron oxide phases decompose, until single phase BaM is left at 1000 °C [78]. Using ethanol as the solvent, iron(III) nitrate and barium metal were heated at 80 °C under N$_2$ to make a sol, which when heated to between 800 and 900 °C gave 150–200 nm BaM. Pure BaM could be formed with stoichiometric mixtures, but the barium had to be between 0.72 and 0.95 wt.% of the precursor sol [79]. SrM has been manufactured by the sol–gel process as a combusted foam and a spray roasted aerosol [80].

The stearic acid gel method is a sol gel method which avoids both coprecipitation and metallo-organic compounds. A stoichiometric mixture of salts are dissolved in melted stearic acid and heated at 80–120 °C/2 h to form a clear sol, which upon cooling forms a homogenous gel intermixed at the atomic level. After combustion of the organic component at 450 °C this results in the formation of nanocrystalline products at low temperatures. BaCo$_2$Ti$_x$Fe$_{12-2x}$O$_{19}, x = 0.6$ with a grain size of 10–20 nm at 750 °C by this process [81]. This has also been used to make more complex hexaferrites, such as Co$_2$X [82] and Co$_2$U [83], at temperatures as low as 750 °C, and with nanocrystalline dimensions.

4.6. Citrate synthesis

Ultrafine particles can be synthesised at low temperatures from decomposed citrates, the decomposition reaction being violently exothermic, in which generation of CO$_2$ results in a very porous product with a high surface area. This is also known as the Pecchini process. To make BaM, a stoichiometric solution of metal salts was mixed with citric acid in a ratio of cation:citrate = 1, and ammonia added to raise the pH and form a homogenous solution. This was heated to 80 °C to drive off any ammonia remaining and added to ethanol to form an iron/barium/citrate complex which precipitated out due to alcohol dehydration, and this was then dried and decomposed at 425–470 °C/48 h. This amorphous product, with a very small grain size of under 10 nm, was then heated to 600 °C to give BaM, although a temperature of over 700 °C was required to obtain a fully crystalline sample with good magnetic properties and a grain size of 60–80 nm [84]. Nanocrystalline SrM particles with a diameter of...
42 nm have also been made from this technique at 800 °C [85]. Co₂Z ferrite was made from citrates that produced a sintered ceramic at only 1150 °C, and was stable up to 1270 °C, with 95% density and good magnetic properties [86].

4.7. Hydrothermal synthesis

In hydrothermal synthesis a solution of metal salts and a base are autoclaved under pressure to give the product. The product is often a mixed phase containing unreacted precursors, and sometimes α-Fe₂O₃, which are removed by washing with dilute HCl. Ataie et al. studied the effects of using NaOH, KOH, (C₂H₅)₄NOH and NH₄OH as bases on the synthesis of BaM and found that NaOH and KOH gave micron-sized BaM platelets at 220 °C/5 h [87]. BaM was also made by autoclaving mixtures of the metal nitrates and NaOH at 332 °C/5 h, which was then annealed at 900 °C to give the pure crystalline product. It was found that an Fe:Ba ratio of 10–12 and an alkali ratio of OH⁻:NO₃⁻ = 2.5–4 was needed to give single phase BaM. Therefore, although this is also a coprecipitation technique the pure phase of BaM can be made from stoichiometric mixtures of barium and iron [88]. More usually, very non-stoichiometric, barium-rich precursor solutions are used, especially to make nanoparticles. In the hydrothermal synthesis of BaM NPs from a γ-Fe₂O₃-Ba(OH)₂ precursor by Drofenik et al., with a very Ba-rich Fe:Ba ratio of 4 and a low concentration of <1 wt% in a weak sodium hydroxide solution, pure BaM was formed at 280 °C/5 h [89]. This was further improved upon by using a Fe:Ba ratio of 5 and a large excess of OH⁻ ions (OH⁻:NO₃⁻ = 12) to make 10 nm BaM NPs at the extremely low synthesis temperature of 150 °C [90]. Hydrothermal SrM was made with a Fe:Sr ratio of 8 [91]. Hydrothermal synthesis has also been used to make more complex hexaferrites, such as Fe₃Y at low temperatures, but it decomposed into BaM and BeFe₂O₄ above 900 °C [92].

4.8. Glass crystallisation

In the glass crystallisation method the ferrite is produced from raw materials mixed with a glass flux, which is then cooled and heated to a temperature below the melting point of the glass to produce the ferrite. A small grain is attainable with this process, as the ferrite is contained within an amorphous glassy matrix, which is then removed with acid to leave the polycrystalline ferrite product [93]. BaM particles made from the glass crystallisation method using fine filaments of B₂O₃ glass produced hexagonal platelets less than 0.1 μm at 800 °C which grew to over 1 μm at 1000 °C [94].

BaCo₀.₇₇Ti₀.₇₇Fe₁₀.₄₆O₁₉ was made from a mixture based on 34 mol% ferrite and 66 mol% glass made from silica or boria. The mixture was melted at 1500 °C and quenched between rollers to give 30 mm flakes, which were then heated at 500–900 °C to produce the ferrite and leached in acid to remove the glass phase. B₂O₃ was found to be the superior glass, with M ferrite crystallising at 642 °C and giving a pure phase product with a grain size of 57 nm, compared to 260 nm at 800 °C with silica [95].

4.9. The combustion method

In a variation on the citrate process, the solution of salts, ammonia and citric acid at pH 7 was evaporated to dryness on a hot plate, at which point a self propagating decomposition occurred. A foamy mass swelled up and ignited in a violent exothermic reaction that propagated through the entire sample in 20 s, as the citric acid polymerised and evolved CO₂ and the cations were completely converted to α-Fe₂O₃ and BaCO₃. The driving force of this extreme exothermic reaction was the combustion of NH₄NO₃ formed in the neutralisation of the solution, and it produced a reaction temperature of 227 °C [96]. The speed of the reaction ensured that homogeneity was maintained and the evolution of gas produced a very porous foam structure that yielded a loose agglomeration when powdered. After firing to 700 °C the sample was mostly BaM with some α-Fe₂O₃ present, and it had formed pure BaM at 1000 °C, but the material has poor magnetic properties, probably because of the small grain size resulting in poor magnetic ordering [97]. This citrate-combustion process can proceed via direct combustion of an aqueous gel containing sufficient levels of oxidiser (Aqueous Combustion Synthesis, ACS) or the ignition of a dried citrate gel powder (Low-temperature Combustion Synthesis, LCS) [98]. It was found that a ratio of citrate:metal ions of ≲0.68 was required to enable the wet gel to
ignite at 200 °C for the ACS method, and that for a ratio of 1:1 the gel had to be dried for 18 h at 120 °C for combustion to occur (LCS). This was because higher levels of citric acid absorbed more water via hydrogen bonding, inhibiting the reaction. A scheme for this process is shown in Fig. 15. Other organic reducing agents have also been used, such as tetraformaltrisazine (TFTA, C₄H₁₂N₆) and oxalic acid dihydride (ODH, C₂H₆N₄O₂), which spontaneously ignite on dehydration and produce higher temperatures over 300 °C, to yield BaM with a grain size of 0.2 μm and good magnetic properties at 850 °C [99]. Microwave heating can be used to induce combustion as well, where the interaction of the microwaves with the materials itself generate the heat, usually at 2.45 GHz, the frequency at which domestic microwave ovens operate. Single phase BaM nanopowders (50–100 nm) were obtained by stirring a stoichiometric mixture of nitrates with citric acid in ethylene glycol (Acid:Fe = 1.5) and ethylene diamine tetraacetic acid (EDTA:Ba = 1.5), adjusted to pH 6.5 with ammonia solution, and with an excess of the amount of ammonium nitrate required to oxidise all the chelating hydrocarbons. This mixture was then freeze-dried, and auto combusted in a microwave oven, with a specially designed quartz vessel and sintered ferrite support to maximise the heating conditions. This complicated preparation resulted in single phase BaM nanopowder being formed directly from the auto combustion reaction [100].

4.10. Self-propagating high temperature synthesis (SHS)

In this method once the reaction has been started, usually by a hot filament, the reaction enthalpy drives the self-energetic reaction to completion. A propagation wave spreads out through the material away from the initiation point at a velocity of 2 mm s⁻¹, causing rapid heating and cooling. SrM was formed from a mixture of SrO₂, which acted as the internal oxidising agent propagating the reaction, and Fe₂O₃ which absorbs some of the energy of the reaction, reducing the synthesis temperature from 2110 °C to 950 °C and preventing the explosive ejection of material from the reaction sites. The pure SrM was then annealed at 1200 °C to give a 1–2 μm product which had mediocre magnetic properties [101]. Co₂Z has also been made by this process from a gel precursor, producing grains several hundred microns in diameter with reasonable magnetic properties, but the Z phase only forming at 1200 °C after initial formation of the M, α-BaFe₂O₄ and Y phases in the SHS step [102].

A recently developed variation is the Carbon Combustion Synthesis of Oxides (CCSO), which involves the exothermic oxidation of 5 nm carbon NPs (“carbon acetylene”) to generate a self-propagat-
ing thermal wave that passes through a mixture of solid reactants. The carbon is not incorporated into the products, and is emitted as CO₂ after reacting with O₂ in a reaction with an enthalpy of −393 kJ mol⁻¹ [103]. This has recently been used to make BaM [104].

4.11. Spray drying

Fine hollow spheres of BaM have been made from the aerosolisation of a solution of metal nitrates, which was atomised and sprayed in a N₂ gas flow into a heated zone for only one second, after which the mainly amorphous spheres were collected [105]. These hollow spheres were under 0.1 μm in diameter, and they formed pure BaM with further annealing but had poor magnetic properties [106]. An industrial method of manufacture is from the freeze drying of iron(III)oxalate and barium acetate in cold pentane [107]. Highly homogenous 0.1–0.3 μm spheres of BaCoₓTiₓFe₁₁.₆–₂ₓO₁₉ (x > 0.8) have also been produced by spray drying a sol–gel precursor, forming the ferrite phase when subsequently heated to 850 °C [108].

4.12. Water-in-oil microemulsions

A microemulsion is a dispersion of two immiscible liquids stabilised by an interfacial film of surfactant molecules, resulting in 5–10 nm domains of one liquid in the other. In this case aqueous droplets are dispersed in an organic solvent, and they continuously collide, coalesce and then break apart again, mixing and exchanging their solute contents. If two microemulsions are mixed which are identical except that they carry different reactants in each aqueous phase, upon collision and mixing the reaction can take place to give nanoparticles, and the morphology can usually be controlled better than in normal coprecipitation [109].

This elegant method of controlled precipitation has been applied to BaM by using a stoichiometric metal salt solution and ammonium carbonate/sodium hydroxide solution as the two aqueous phases, to give a nanosized iron–barium–carbonate/hydroxide precipitate which was then separated, washed and dried. BaM forms over 600 °C and is single phase at 925 °C, with control of grain size over the range 120–170 nm [110].

4.13. Industrial manufacture of hexagonal ferrites

The raw materials used to manufacture commercial M ferrites are α-Fe₂O₃, either natural or synthesised from iron pyrite (FeS₂), iron chloride or organometallic pigments, and barium or strontium carbonates. Ferrites can be made from iron oxides recovered from waste steel pickling liquors, a cheap source of raw material in a sulphuric acid liquor with a high Fe²⁺ content. Goethite, haematite and magnetite have all been recovered successfully [111], and BaM with very good magnetic properties has been manufactured from the iron oxide recycled materials [112,113]. The iron oxides are granulated, mixed and presintered to form the M phase, milled again to improved homogeneity, pressed to increase density and sintered at up to 1400 °C [114].

In the dry milling of BaM, Mₛ and Hₐ are decreased with milling time because of two factors, an increase in lattice distortions from the induced stress and the formation of the magnetically weak BaO and α-Fe₂O₃ phases. Milling the material in a low oxygen pressure or a vacuum can reduce the second effect. Wet milling lowers the energy and gives a stress free powder, removing the source of lattice distortions and preserving the structure of the M ferrite, but it also increases the rate of particle size decrease and after 60 h M decomposes to the oxides. With increasing milling time Hₐ increases and Mₛ and M_r decrease as the particle size is reduced, but if surfactants are added to the liquid a large Hₐ value is still obtained but the decrease of M_r is lessened and a material with a square loop and higher energy results [115]. The ball milling of hydrated Ba(OH)₂ and Fe₂O₃ in a hydrophilic solvent encouraged the formation of micro-agglomerates enhanced the homogeneity and reactivity of the components, which sintered easily [116].

Ferrites can be granulated by the vacuum hot steam process, which gives a drier, denser, more homogeneous and more abrasion resistant material than other granulation processes. The ceramic is first homogenised and mixed in a high speed mixer by shearing forces, and then granulated by
drying under vacuum as superheated steam is passed through the material [117]. In rubber isostatic pressing M ferrite with a small addition of calcium stearate is pressed in an external magnetic field and then sintered. This gives a highly dense (~5 g cm\(^{-3}\)) material with improved magnetic orientation, and if a fine grained ferrite is used both \(M\) and \(H_c\) can be optimised. For a high \(M\) material, 0.7 \(\mu\)m SrM with 1 wt.% calcium stearate is fired to 1240 °C to give a 99% oriented material with a coercivity of 239 kA m\(^{-1}\), and for a high \(H_c\) ferrite 0.3 mm SrM powder has 2 wt.% stearate added, and the ferrite fired at 1200 °C to give a 96% oriented material with a coercivity of 238.7 kA m\(^{-1}\) [118]. The optimum mixture, to make a 71% SrM plastoferrite with 99% orientation by injection moulding, was found to be 95–98% 2–3 \(\mu\)m grains with 2–5% 100–600 nm grains [119].

A simple method of making small grain, high coercivity ferrites is mechanochemical processing, in which mixtures of iron and barium chlorides, in a non-stoichiometric ratio of Fe:Ba = 10, and a large excess of NaOH are milled together. A chemical reaction is induced giving a homogeneous mixture of metal oxides/hydroxides and NaCl, which can be washed out after the powder has been annealed at 800 °C to give BaM grains 100 nm wide and 20 nm thick [120]. Ferrites with a high length to diameter ratio are usually made by extrusion or isostatic pressing [121]. Flat bars and sheets of pure BaM are made by pressing the dense pre-sintered ferrite perpendicular to the direction of extrusion, to give a material with a grain size of 0.5–1.3 \(\mu\)m [122], and monodisperse powders are produced by spray drying [123].

5. The solid state chemistry of the hexagonal ferrites

Many studies have been made of the solid state reactions of the BaO–Fe\(_2\)O\(_3\)–MeO system using standard ceramic preparations from oxides and BaCO\(_3\). M.A. Vinnik constructed several phase diagrams (Fig. 16) and obtained the X-ray spacings of BaM, Y, Z and W for samples containing more than 50% Fe\(_2\)O\(_3\). In samples which were heated to 1200 °C/2 h, pressed and then annealed at 1250 °C/4 h, no Co\(_2\)X or Co\(_2\)U could be detected even at their stoichiometric compositions in polycrystalline samples [46]. Also changes in the lattice parameters for compositions near the borders of the Z and W regions in the phase diagram suggested that M, Y and W can dissolve in Z, and M dissolves in W better than Y or Z, to form solid solutions at these border compositions. The magnetic hexagonal ferrites are often mixed with BaFe\(_2\)O\(_4\) which is also hexagonal but non-magnetic, but this can be removed by dissolving in HCl, as the other phases dissolved much more slowly [18]. It was also found to be extremely difficult to produce a single phase sample of polycrystalline Y, Z or W ferrite, and the first sample produced had

![Fig. 16. The BaO–Fe\(_2\)O\(_3\)–MeO phase diagram by Vinnik [46].](image)
to be reduced to a single phase by grinding the grains down [18]. Single crystals several mm long of Co$_2$Y and Fe$_2$W could easily be grown by the flux method, but the higher melting Co$_2$W, Z, X and U ferrites were more difficult to produce [124].

As can be seen in Fig. 17 from the study by Neckenburger, Severin et al., many of the different phases involved coexist at the same temperatures, and all of the hexagonal ferrites overlap [45,125]. $\alpha$-Fe$_2$O$_3$ has a peak wt.% of 65% at 700 °C, the spinel phase peaks at 5% at 700–900 °C, BaFe$_2$O$_4$ has a peak of 25% at 800 °C, BaM = 75% at 800 °C, Y = 60% at 1100 °C, Z = 85% at 1300°C and W = 60% at 1400 °C. The X and U phases are often indistinguishable from this background of mixed phases, and as the hexagonal ferrites share the same basic building blocks in their structures, their X-ray diffraction patterns and magnetic characteristics are often very similar as well. It must also be remembered that this data is for a non-stoichiometric mix of oxides, and that an accurate stoichiometry for the desired hexagonal composition in the starting materials improves the yield of that phase, often enabling a single phase product to result. At temperatures over 1350 °C Fe$^{3+}$ is reduced to Fe$^{2+}$, and this forms the solid solution Co$^{2+}$Fe$^{2+}$Fe$^{3+}$O$_4$ which leads to the decomposition of the Y, Z and W phases [46]. Lotgering named the process by which the more complex hexaferrites form from a rearranging of other plate-like hexaferrite precursors a topotactic (or topotactical) reaction, and used this technique to produce oriented polycrystalline crystals by reaction of the oriented grains of BaM with non-oriented grains of other non-magnetic components, to make oriented W, Y, Z and substituted M ferrites [126]. This may partially account for the extreme step-like formations observed in many hexaferrite ceramics by many authors (e.g., Fig. 18).

A detailed investigation into the formation of M, Y, Z and W ferrites was also undertaken using co precipitated precursors by Castelliz et al. [21]. Nitrate salts were mixed with ammonium oxalate and stirred in solution under an IR lamp until a critical concentration was reached, at which point the simultaneous precipitation occurred, resulting in an intimate mixture of already partially decomposed oxalates. These were then decomposed fully at 500°C, ground, calcined at 800°C, ground, pressed, and finally fired at 1100–1400 °C. The spinel phase was seen to form at 650 °C and the BaM phase at 800 °C, both remaining until over 1100 °C. Manganese spinel ferrites are atmosphere sensitive at high temperature, and MnO and Mn$_2$O$_3$ can precipitate out of the ferrite if the partial pressure of oxygen is lowered [127]. Sudakar et al. made a highly detailed study of the BaO–NiO–Fe$_2$O$_3$ system synthesised from a complex reaction of coprecipitated reactive gels at 80–90 °C, which produced nanopowder precursors which all contained the relevant hexaferrite phase when heated to 750 °C, and all formed the single phase M, Y, Z, W, X or U ferrite when heated to 950 °C [25]. The precise details of each are discussed in their relevant section. In the same article, they also studied the crystal structure of the
ferrites by TEM, and while they exhibited the expected, and mostly defect free, stacking sequences at 950 °C, they observed major ordering changes in the stacking of the component M, Y and S layers in Ni$_2$Z, Ni$_2$X and Ni$_2$U ferrites when heated above 1350 °C.

5.1. BaM ferrite

The BaO·Fe$_2$O$_3$ system was first investigated in depth in 1946 [128], and in this and other early studies found many contradictory results, with the hexagonal BaFe$_2$O$_4$ phase sometimes being reported as coexisting with $\alpha$-Fe$_2$O$_3$ up to 1400 °C, and sometimes not forming at all. The confusion may have arisen from other metastable phases that have since been identified. BaM and BaFe$_2$O$_4$ are mutually insoluble in each other as solids [129], and both form from 650 to 1000 °C, after which point a third phase can also develop until the ternary mixture reaches its liquidus point at 1175 °C. This third phase was identified as the metastable hexagonal Ba$_2$Fe$_6$O$_{11}$, which is stable up to its melting point of 1350 °C, reverting to BaM and BaFe$_2$O$_4$ on cooling [130]. In standard ceramic preparations the hexagonal BaFe$_4$O$_7$ phase can coexist with the BaM and BaFe$_2$O$_4$ phases below 1000 °C [131], and there are also two different phases of BaFe$_2$O$_4$, $\beta$-BaFe$_2$O$_4$ existing up to 1000 °C and $\alpha$-BaFe$_2$O$_4$ over 1000 °C [132]. BaM crystallisation was found to have an activation energy of 73.2 kcal mol$^{-1}$ at temperatures above 735 °C [133]. Often BaCO$_3$ exists in crystalline form as a precursor, either as a starting material or a decomposition product, and if present this needs to decompose between <700 °C before barium ferrites can form [52].

The products of BaCO$_3$ and Fe$_2$O$_3$ heated at 750–1200 °C and in the ratios of Fe:Ba of 2–12 were thoroughly investigated in 1973, and it was found that this ratio greatly affected the products. In all ratios, BaM and BaFe$_2$O$_4$ coexisted below 1000 °C until they reacted to form Ba$_2$Fe$_6$O$_{11}$ over this temperature, but from 1000 °C to 1150 °C the products were Ba$_3$Fe$_6$O$_{11}$ and BaFe$_2$O$_4$ for the ratios 2–3, and BaM and Ba$_2$Fe$_6$O$_{11}$ up to a ratio of Fe:Ba = 12. The BaFe$_4$O$_7$ phase was never observed, and all mixtures decomposed back to BaM and BaFe$_2$O$_4$ over 1150 °C [132]. There is much ambiguity over the precise compositional solid solution range in which pure BaM can exist, with claims varying from an Fe:Ba ratio of 10–12 [131] to 11.4–2 [129,134] 11.6–12 [135] or only at exactly 12 [136]. Sometimes it almost seems as though it is easier to make the more complex hexaferrites from their stoichiometric precursors than the M ferrites. Another phase has been identified between 600 and 950 °C as BaO·nFe$_2$O$_3$ where $n = 4$–5.8, which has a very similar XRD pattern to the M ferrite, which may explain some of these apparent discrepancies [137]. Lipka et al. claimed that the optimal Fe:Ba ratio for a cit-
rate gel is 10.8, starting to form at 600 °C and being single phase at 950–1100 °C, analysing the phases by Mössbauer spectroscopy, with α-Fe₂O₃ and α-BeFe₂O₄ being reported as the secondary phases when above or below this ratio [138]. Pullar et al. demonstrated that single phase SrM and BaM could be made from stoichiometric aqueous sol–gel precursors, stabilised by either halide or nitrate counterions [71,72,77]. Furthermore, they showed that neither BaFe₂O₄ nor γ-Fe₂O₃ is necessary as a pre-cursor phase, with the amorphous FeOOH-based sols crystallising into α-Fe₂O₃ by 400 °C which then transformed directly into the M ferrite at 600–700 °C, resulting in single phase SrM and BaM between 700 and 1000 °C [139]. Rapid grain growth occurs above 1200 °C leading to DGG [140], and BaM melts around 1500 °C, dissociating to the W and X phases [141].

As can be seen from the phase diagram of the ternary system (Fig. 16), M ferrite forms in regions clustered around the stoichiometric point to make the intermixed phases M + α-Fe₂O₃ M + W, M + Z, M + W + Z, and the pure phase is formed around 14.3% BaO–85.7% Fe₂O₃ [45]. The rate of the solid state reactions can be enhanced by radiation effects, and the radio stimulated diffusion of Fe, Mn and Zn ions is more than an order of magnitude faster than thermal diffusion in ferrite synthesis [142].

M ferrites produced from standard ceramic methods typically shrink by 20% in linear dimensions during sintering and densification, and a further 1% upon cooling, and this is also true for magnetically isotropic bulk specimens with no magnetic alignment of the individual particles. In magnetically anisotropic samples however, in which the grains are all oriented with their c-axes parallel, the shrinkage is also anisotropic during sintering, typically 23% parallel to the c-axis and 11.5% perpendicular to it [143].

As BaM is the most commercially important hexagonal ferrite, its solid state chemistry has been studied in much greater detail than that of the other hexagonal ferrites. The differences in reaction and product are highly dependent upon the manufacturing process employed, and these differences are summarised below.

5.1.1. Coprecipitated BaM

In coprecipitated BaM ferrite an iron-deficient non-stoichiometric mixture is normally needed, usually with an Fe:Ba ratio between 10 and 11, to form the single phase product [51], and sometimes ratios as low as 8 are reported as being optimum [144]. The dried hydroxide coprecipitates FeOOH and Ba(OH)₂ go through an endotherm between 130 and 350 °C as water is lost and the hydroxides are decomposed to oxides, but the material remains amorphous until BaM starts to form at 700 °C, with no crystalline precursors. Mₜ begins to increase at this point as the M phase crystallises, and there is a sharp exotherm at 760 °C corresponding to this crystallisation. The heating rate of 10 °C/min used in differential thermal analysis (DTA) leads to an artificially high temperature value for rapid processes, such as crystallisations. The material is all converted to BaM at 900 °C and grain growth occurs over 1000 °C. No phases other than BaM were reported [52]. In a variation an iron(II) salt is used instead to produce the precipitate Fe(OH)₂ which has a sparse structure, and 70% of the Ba²⁺ ions are contained within this, not as separate Ba(OH)₂ molecules [145]. Normally the iron(II) precipitate will slowly oxidise to iron(III) by redissolving and precipitating as α-FeOOH, the form of iron(III) hydroxide that is usually formed from iron(III) salts. This is too dense to keep the Ba²⁺ ions within its structure, but if the intimate mixing could be maintained in an iron(III) hydroxide long range diffusion would not be needed to form BaM, and lower reaction temperatures would be needed. This can be achieved by vigorous oxidation of the Fe(OH)₂ precipitate with H₂O₂ which bypasses the dissolution/reprecipitation step entirely by simply extracting part of the hydrogen from Fe(OH)₂ to give δ-FeOOH. Ba²⁺ ions are retained within, but it also has a hexagonal structure and so it acts as a good template for BaM formation. At 300 °C δ-FeOOH dehydrates to form a poorly crystalline barium-doped α-Fe₂O₃ which still retains the barium ions even when it becomes fully crystalline at 550 °C, and as a result of this atomic scale mixing the activation energy of BaM crystallisation is lowered. The barium-doped α-Fe₂O₃ is also less thermodynamically stable and so single phase BaM is formed at a very low temperature of 600 °C with a grain size of 80 nm. The c parameter is 0.02% smaller than expected, and it is suggested that M structure is not fully developed at this point as the five-coordinate Fe³⁺ site does not exist in haematite, but the material has the exact BaM cell length at 700 °C [56].

Lisjak and Drofenik investigated the mechanism of BaM formation from a stoichiometric co-precipitated precursor using both nitrates and chlorides with NaOH, and then calcined between 300 and
800 °C for up to 50 h [146]. They found that \(\alpha\)-Fe\(_2\)O\(_3\) crystallises at \(-290\) °C, and that BaCO\(_3\) forms from a reaction of some (not all) of the Ba(OH)\(_2\) with air. Below 500 °C their was no evidence of BaM formation, but it begins to form from amorphous precursors at 500 °C. Then at 600 °C and above BaCO\(_3\) reacts with \(\alpha\)-Fe\(_2\)O\(_3\) to form BaFe\(_2\)O\(_4\), which in turn reacts with more \(\alpha\)-Fe\(_2\)O\(_3\) to form BaM — this is so rapid, that after 700 °C/30 min no BaFe\(_2\)O\(_4\) was present. In DTA measurements a crystallisation of BaM was observed at 633 °C, but this is thermodynamic process and with longer firing times it can occur at lower temperatures around 600 °C. This demonstrates that there are two distinct steps to the formation of BaM — even after 500 °C/50 h the co-precipitated powder had not fully transformed to BaM, as the portion of barium which was carbonate could not react at this temperature, but after 600 °C/5 h or 700–800 °C/1 h it was all BaM. This two stage process, crystallising from both amorphous and crystalline precursors, leads to a broad particle size distribution, from nm sized irregular particles to hexagonal plates >100 nm diameter. A recent study of the precipitation of FeOOH at pH = 3–9 followed by BaCO\(_3\) at pH 9 was carried out by Pashlova et al., using stoichiometric mixes of salts and ammonia. They found that varying the pH between 3 and 9 for Fe\(^{3+}\) precipitation had virtually no effect, and that BaM began for form at 800 °C, and was the major or only phase at 950 °C [147]. The measured the effects of pH on composition and % BaM yield, the fractal dimension of the gel, BaM particle size, and magnetic properties (Fig. 19). It was found that the optimal pH for FeOOH precipitation to make high purity BaM was 4.3, which coincided with the minimal fractal dimension of the dried gel, and a larger final BaM particle size when calcined at 950 °C. These were monodisperse hexagonal platelets, with good magnetic properties.

Lisjak and Drofenik have also investigated the use of ethanol instead of water as a solvent during coprecipitation, to avoid problems of absorbed CO\(_2\) from the atmosphere in water forming BaCO\(_3\) [148]. They used stoichiometric iron ratios for chloride and acetate salts precipitated with NaOH in a 3:1 ethanol:water solution, both in air and under a flow of Ar. They found that with chloride precursors coprecipitated in both air and Ar, BaM had crystallised as low as 500 °C/10 h, although also with poorly crystalline \(\alpha\)- and \(\gamma\)-Fe\(_2\)O\(_3\) present, and it formed the pure BaM phase at 600 and 700 °C/10 h respectively, for the samples coprecipitated in Ar and air. The sample made using acetates under Ar had a similar crystallisation, but become single phase BaM only at 700 °C, while the sample made from acetates in air was the only one to form BaFe\(_2\)O\(_4\) as a precursor, and although BaM began to crystallise

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**Fig. 19.** Top table: Effects of pH of FeOOH precipitation on phase composition at various firing temperatures for coprecipitated BaM precursors (BHF = BaM). Plot a: % yield of BaM (left axis) when calcined at 800 °C (2) and 950 °C (1), and fractal dimensions (right axis) of the gel died at 18 °C (3) and 120 °C (4), respectively. Plot b: final particle diameter with pH of FeOOH precipitation, when calcined at 950 °C (1) and 1000 °C (2). Plot c: magnetisation loops of powders calcined at 1000 °C, prepared at various pH values [147].
at 600 °C/1 h, it never became the single phase in this sample until 800 °C/3 h. Therefore, it was clear that formation of BaFe$_2$O$_4$ delayed the full crystallisation of BaM, and that either an Ar atmosphere or the presence of chloride salts prevented the formation of BaFe$_2$O$_4$. This was attributed to an enhanced diffusion rate in calcining due to the flux of NaCl (a side product of the coprecipitation from chlorides), and by the improved homogeneity of the precipitates due to additional stirring by the Ar flow bubbling though the solution. An activation energy was calculated for the crystallisation of BaM as being 50 kcal mol$^{-1}$, in both air and under Ar. When sintered to 700 °C/1 h, the BaM samples had low $M_I$ values <60 A$^2$ m$^2$ kg$^{-1}$, but all had high $H_c$ ~ 400 kA m$^{-1}$, due to the small grain size of the particles (≤100 nm). Although no BaCO$_3$ was detected in the fresh precipitates, this was not true for precipitates exposed to air for a day or more, suggesting that the amorphous Ba-precursor reacted with the CO$_2$ in the air over time to form the carbonate. In a later paper they concluded that to make BaM at a low temperature of 500 °C it was best to use co-precipitates made with chloride salts in ethanol, although firing to 600–700 °C was need to obtain the optimum magnetic properties [149].

A novel approach was coprecipitation from an alkaline sodium ferrate(VI) solution with barium chloride, which crystallised BaFe$_2$O$_4$ and BaM from the amorphous precursor at 620 °C, and formed the single phase M ferrite above 710 °C with submicron grain sizes and reasonable magnetic properties [150,151]. Sudakar et al. formed BaM from a thermal gel-crystallisation process that crystallised single phase M ferrite (grain size <100 nm) directly from a stoichiometric precursor at 750 °C, with γ-Fe$_2$O$_3$ seen as a transient intermediate phase at 650 °C [25].

5.1.2. Salt-melt process for BaM

In an investigation of the salt-melt process the coprecipitated precursor powder was shown to be a mixture of crystalline α-FeOOH in the form of 50–100 nm hexagonal platelets and amorphous agglomerates of Ba(OH)$_2$ and Fe(OH)$_3$. This fine precursor then forms even finer α-Fe$_2$O$_3$ with a grain size of only 40–50 nm, and BaM begins to crystallise at 638 °C, possibly because the hexagonal template acts as a template for topotactic BaM formation [152]. After being heated to 1000 °C/4 h in a NaCl/KCl flux and separated from the alkaline metals the product was pure BaM with a wide range of grain diameters between 0.2 and 1.5 μm. If a flux containing only NaCl was used the single phase ferrite could be made with 300 nm grains after only 850 °C/1 h while retaining excellent magnetic properties, and Co–Ti or Zn–Ti doping further reduced both the grain size to 50–150 nm and the size distribution [60]. An ammonium nitrate based melt technique has also been used to make BaM, which is formed on subsequent calcination at 1000 °C, and separated by subsequent washing with HCl. The calcined products of this method are a mixture of BaM and either BaFe$_2$O$_4$ (for ratios of Fe:Ba of 2–6) or α-Fe$_2$O$_3$ (for ratios of Fe:Ba of 7–13). BaFe$_2$O$_4$ can be easily removed by washing with HCl to leave the BaM product, so highly non-stoichiometric, low Fe:Ba ratios are preferred [153].

A variation of this process uses a higher melting mixture of NaCl and B$_2$O$_3$ in smaller quantities so an incomplete flux is achieved, and the rate of formation is closer to that of normal solid state diffusion. With this technique 250 nm particles of BaCoTiM were produced at 980 °C/1 h, so it does not seem to have any advantage over the full melt flux process [62]. However, if the melt-flux is heated radiothermally with an electron beam the single phase ferrite is produced at a lower temperature of 900 °C as platelets below 100 nm in diameter and of reduced thickness [63]. In all of these techniques an iron deficient stoichiometry is needed to form the pure M phase, as in the purely coprecipitated materials.

5.1.3. Sol–gel synthesis of BaM

Even when BaM was made from a sol–gel route involving the evaporation of a sol containing coprecipitated salts and glycol to give a homogeneous gel, it was still found that a non-stoichiometric mixture was needed, and a ratio of Fe:Ba of 10.5 gave M ferrite at 900 °C/1 h with a grain size of only 200 nm [68]. Only the barium rich precursor yielded pure M without any α-Fe$_2$O$_3$ as a second phase, but with a ratio of less than nine BaFe$_2$O$_4$ appeared as a secondary phase instead [69], indicating that there is only a narrow compositional window for the formation of BaM by this method. When the Fe/Ba ratio was fixed at 11.6, and BaM was made from either nitrate or hydroxide sol–gel precursors, it was found that the presence of the nitrate anion was an important factor in the formation of the intermediate phases α-Fe$_2$O$_3$ and BaFe$_2$O$_4$ over a wide range of temperatures. Elimination of these
non-magnetic phases was achieved by preheating the gel at 450 °C/5 h to eliminate any organic compounds, with BaM forming at 750 °C, although the best magnetic properties were obtained at 950 °C BaM [96].

Investigations into an acidic sol made with a citrate coordinating agent revealed that the prefireing of the gel at 450 °C/5 h to remove the organic component is a crucial step, reducing the formation temperature of pure BaM from 1050 °C to 750 °C, and consequently the grain size. Without the prefireing step, when heated directly at a rate of 4.5 °C h⁻¹ BaM began to form at 550 °C, but coexisted with α-Fe₂O₃ until the single phase product resulted at 750 °C. At 900 °C this had an average grain size of 129 nm, but it was found to consist of two distinct phases, 20–30 nm spherical α-Fe₂O₃ and 500 nm hexagonal BaM. With prefireing BaM started to form at the higher temperature of 650 °C, but α-Fe₂O₃ never formed, and the product’s average size was 101 nm, consisting of homogeneously sized hexagonal platelets between 90 and 110 nm. BaFe₂O₄ was present as a minor phase in both specimens between 650 and 750 °C. The determining factor was found to be the γ-Fe₂O₃ phase, which was present in both specimens at 500 °C but decomposed to α-Fe₂O₃ without prefireing. In the prefired samples the γ-Fe₂O₃ was more crystalline before BaM formation, and the deficient cubic spinel structure (Fe₁₋ₓFeₓO₄) resembles the S block and therefore may easily react with BaFe₂O₄ to form BaM [70]. BaM made by the stearic acid gel method formed as a single phase at 650 °C [81]. In a study of the effect of various acid catalysts on the gelling of nitrates (Fe:Ba = 10:5), the organic stearic and acetic acids where found to be most successful, producing pure BaM upon calcination at 700 °C and above. Acetic acid gave large grain of ~5 mm, while stearic acid produced fine, submicron powders at 1000 °C [154].

The synthesis of BaM from an organic sol–gel precursor has been studied by neutron powder diffraction. All the organic compounds were removed at 420 °C to leave crystalline γ-Fe₂O₃ as the major phase up to 680 °C, the crystallites growing from 15 nm at 150 °C to 30 nm at 600 °C. At this temperature BaCO₃ appears out of the amorphous background, and α-Fe₂O₃ and BaFe₂O₄ form soon afterwards. BaM forms at 680 °C as the γ-Fe₂O₃ decomposes, along with the other iron phases, until single phase BaM is left at 1000 °C. It is suggested that the Ba²⁺ ion moves into the cation-deficient spinel structure of γ-Fe₂O₃ [78]. In an ethanol based sol made from iron(III) nitrate and barium metal it was found that to form pure BaM the barium had to be 0.72–0.95 wt.% of the sol, and again γ-Fe₂O₃ and BaFe₂O₄ appeared to be essential for the formation of BaM at 800 °C with a grain size of 150–200 nm [79].

In their investigations into an organic-free, aqueous sol–gel based system, Pullar et al. showed that BaM and SrM can be produced from stoichiometric precursors [71,72]. No BaFe₂O₄, γ-Fe₂O₃ or any other ferrite intermediate was observed in the M ferrite precursor powders, with the M ferrites forming directly from α-Fe₂O₃ only [139], except in the case of BaM made from a halide stabilised sol, where crystallised barium halide salts were also observed. This suggested that the initial formation of γ-Fe₂O₃ or BaFe₂O₄ are not necessary for the formation of M ferrites, although there was some doubt that the presence of halides may have inhibited the formation of these precursors. Although halide-based sol precursors had been shown to be more stable, it was also seen that the halides persisted until high temperatures (~10 wt.% at 600 °C), particularly chloride ions, delaying the onset of BaM formation until 750/800 °C for SrM/BaM, and the single phase M ferrites were not obtained until 900/1000 °C, at which point there was no halide remaining in the powder. This coincided with a weight loss of 4–5% between 800 and 1000 °C, as the halides were driven off [155]. By contrast, in halide-free sol precursors based on nitrates, the ferrites began to form directly from α-Fe₂O₃ at lower temperatures of 650 °C for BaM, becoming the single phase at 750 °C, and no crystalline nitrate precursors were observed. In halide-free SrM the transition was even more rapid, from α-Fe₂O₃ at 650 °C to single phase SrM at 700 °C [139], absolutely proving that γ-Fe₂O₃ or BaFe₂O₄ are not essential precursors to the formation of the M phase.

ICI and Sumitomo have both used steaming processes to remove chlorides from aluminosilicate fibres, and investigations were made into halide removal from BaM and SrM fibres made by the halide-based aqueous sol–gel process via steaming during crystallisation and sintering. It was found that in the steamed fibres the M phase began to crystallise at 600 °C, and they became single phase SrM and BaM at only 700 °C, confirming the inhibitory effect of associated halides on ferrite formation [156]. The steamed ferrites sintered at 700 °C also had a much reduced grain size <100 nm compared to
the previous M ferrite fibres heated to 1000 °C, but similar magnetic properties. This agrees with other findings: a small amount of chloride retained in M ferrite powders at high temperatures has been shown to encourage grain growth, and levels up to 1 wt.% have also been claimed to promote crystallisation and inhibit shrinkage [157], and in M ferrite powder which was heated at 1200 °C in an oxygen atmosphere, 80% of the residual chloride was removed, and a product with a grain size of only 0.5 μm was made [158].

5.1.4. Hydrothermal synthesis of BaM

The has been a recent increase in interest in the hydrothermal synthesis of hexaferrites, as it is a relatively economic and simple way of making ferrite nanoparticles (NPs). Although the as-synthesised product contains hexaferrites NPs at synthesis temperatures <250 °C, it is often a mixed phase or chemically inhomogeneous, and usually needs subsequent annealing to make a pure phase hexaferrites product. Despite this, extremely planar hexagonal ferrite NPs often result, with a very high diameter:thickness ratio of the platy hexagonal grains, making them ideal for orientation and texturing. Up to now, nearly all of the research into hydrothermal synthesis of hexagonal ferrites has concentrated on M ferrites, and the process is quite different to that of other wet chemical or ceramic techniques carried out in ambient conditions. It would seem that a non-stoichiometric, iron-deficient precursor is usually necessary to form good NPs, and usually to a more extreme extent than for other methods. Despite this, it has been reported that pure phase BaM can be made from stoichiometric mixtures of iron and barium by hydrothermal synthesis. However, the product is poorly crystalline, and must be annealed at 900 °C to allow the Ba2+ ions to diffuse fully from the surface into the M lattice [88]. At ratios below Fe:Ba = 10 the excess barium caused BaCO3 to form as an impurity – such carbonate impurities are often seen in hydrothermal hexaferrites products, as the barium and strontium react with CO2 in the air during the reaction. An early hydrothermal paper found that γ-Fe2O3 and α-FeOOH were better precursors for hydrothermal synthesis of BaM than α-Fe2O3, when autoclaved with Ba(OH)2 at 250–280 °C [159]. They reported that a Fe:Ba ratio of 6 was needed to make nearly-single phase BaM, and at other ratios they detected Ba3Fe8O15, which is always present when α-Fe2O3 was used.

X. Liu et al. reported that a Fe:Ba ratio of 8, OH− : NO3− ratio of 2, and a reaction at 230 °C/48 h was required to make best quality single phase BaM [160]. In this paper they also investigated the variation of OH− : NO3− ratio (1–5), Fe:Ba ratio (8–12) and temperature (200–240 °C) on the hydrothermal synthesis of BaM from nitrates with NaOH. Single phase BaM was made with OH− : NO3− ratios of 2–5 at 230 °C, and as this ratio increased the size of the BaM particles decreased from 1.8 to 1.2 μm. These smaller particles at a ratio of five were less regularly shaped and formed agglomerates 5–10 μm in size, whereas with a ratio of 2 they were well dispersed hexagonal platelets. With a Fe:Ba ratio of 8 (230 °C/48 h) pure BaM formed, with 10 some α-Fe2O3 was present, and with 12 this impurity became the major phase. Particle size increased from 1 to 2 μm as reaction temperature increased from 200 to 240 °C/48 h, and as reaction time was extended at 230 °C BaM became the predominant product after 15 h and then only product after 25 h – higher temperatures required less time to achieve this. BaFe2O4 was never observed in this study. On subsequent firing to 1000 °C the grains grew to regular hexagonal plates 1.5 μm × 150 nm, but remained as discrete grains, although above this temperature they began to fuse and sinter, with DGG occurring. In their early paper, Ataie et al. claimed to have made pure micron sized platelets of BaM using NaOH or KOH as bases at 220 °C/5 h, but do not say what ratio of Fe:Ba was used, which is critical information. When NH4OH or (C2H5)4NOH were used as bases, 10–20 nm particles of α-Fe2O3 were formed, with traces of BaM and BaFe2O4. They also claimed that BaM formed from α-Fe2O3 and BaFe2O4 intermediates [87].

Liu et al. have written a highly detailed paper on the hydrothermal synthesis of BaM and Al3+ substituted BaM, from a mix of chloride and nitrate salts with NaOH solution (2 × excess), and the resulting powders well washed to ensure removal of Cl− [161]. The key to their process is that the spinels Fe3O4 or γ-Fe2O3 will convert to BaM more readily than α-Fe2O3, as they have more similar structures to the M ferrite. They noted that α-Fe2O3 is also more thermodynamically stable, and that a lower temperature process such as hydrothermal will be more favourable towards iron oxide spinel formation. They encouraged spinel formation by using a mixture of FeCl2 and FeCl3 to create a mix of Fe2+ and Fe3+ ions, and they used an initial iron:barium ratio of 11.5. They found that more than
50% Fe$^{2+}$ gave Fe$_3$O$_4$, not BaM, and they found the optimum Fe$^{2+}$:Fe$^{3+}$ ratio to be 2:8, which resulted in mostly BaM with a small amount of $\alpha$-Fe$_2$O$_3$ and no Fe$_3$O$_4$ at 250 °C/25 h. The totally Fe$^{3+}$ precursor gave more $\alpha$-Fe$_2$O$_3$. The stated that a total Fe:Ba ratio of 10.5 was ideal, forming pure BaM after 250 °C/25 h, and that for ratios of 8 or less, BaFe$_2$O$_4$ formed as well, and that a small excess of Ba inhibits $\alpha$-Fe$_2$O$_3$ formation. They then studied the effects of varying synthesis temperature and time, and found that single phase BaM could be formed at 250 °C/2 or 200 °C/4 h, when using a total Fe:Ba ratio of 10.5 and a Fe$^{2+}$:Fe$^{3+}$ ratio of 2:8. The crystals formed as thin hexagonal plates, and as reaction temperature or time was increased these grew and increased in crystallinity (Fig. 20a and b). They also concluded that increasing the reaction temperature or time enabled the use of a higher Fe:Ba ratio or a lower Fe$^{2+}$:Fe$^{3+}$ ratio to produce pure BaM. Their paper contains an excellent summary of much of the previous work carried out on BaM hydrothermal synthesis, which nearly always seems to require a barium excess, especially at lower temperatures, but they also state that a non-stoichiometric excess of barium and the pre-formation of BaFe$_2$O$_4$ is always required in other preparation methods to form BaM – as we have seen above, this is not true. A mixture of BaCl$_2$ and FeCl$_2$ only with KNO$_3$ and NaOH was studied with variation in OH$^{-}$:Cl$^{-}$ ratio, reaction temperature and time for a stoichiometric BaM solution. At 230 °C/10 h with a OH$^{-}$:Cl$^{-}$ ratio of 2, 1 μm diameter hexagonal plates with peak coercivity were produced [162].

Drofenik et al. investigated the synthesis of BaM via hydrothermal synthesis, from a γ-Fe$_2$O$_3$-Ba(OH)$_2$ precursor with very Ba-rich Fe:Ba ratio of 4, and a low concentration of <1 wt% in a sodium hydroxide solution, that contained a massive excess of OH$^{-}$ ions (OH$^{-}$ : NO$_3^{-}$ ≪ 30) [89]. This was heated in a sealed autoclave in a hydrothermal reaction at 280 °C/5 h to form a mixture of BaM and BaCO$_3$, and once BaCO$_3$ was removed by washing with acid, only pure BaM NPs remained. However, BaFe$_4$O$_7$ tended to form if Fe:Ba <4, and $\alpha$-Fe$_2$O$_3$ if >4, and they also found that when the solution was diluted to less than 1/4 of the original concentration, BaFe$_4$O$_7$ formed as well. In such a non-stoichiometric reaction it seems strange that BaM should be formed at all as a major phase, as it relies on

Fig. 20. SEM images of hydrothermally synthesised M ferrites. (a and b): BaM with Fe:Ba ratio of 10.5 and Fe$^{2+}$:Fe$^{3+}$ ratio of 2:8, reacted at (a) 200 °C/4 h and (b) 250 °C/4 h. (c and d): BaFe$_{11.3}$Al$_{0.7}$O$_{19}$ with (Fe + Al):Ba ratio of 9.5 and Fe$^{2+}$:Fe$^{3+}$ ratio of 2:8, reacted at (c) 230 °C/4 h and (d) 250 °C/4 h [161].
12 Fe ions reacting with one Ba ion. The reaction was based on $\gamma$-Fe$_2$O$_3$ being amphoteric, and reacting in a strongly alkaline environment to form the tetrahydroxoferrate ion Fe(OH)$_4$ (instead of the FeOOH more commonly seen in hydroxide-based sol–gel synthesis). This tends to form iron rich aggregates, [Fe(OH)$_4$]$^{x-}$, with $x$ (the size of the aggregates) depending on the OH$^-$ concentration. This can react with Ba to form either BaM or BaFe$_4$O$_7$, with Fe:Ba ratios lower than 4 favouring BaFe$_3$O$_7$ formation, but a ratio of 4 with a larger OH$^-$ excess favours [Fe(OH)$_4$]$^{x-}$ complex ions big enough to produce BaM. The reason why dilution beyond a critical point also yielded BaFe$_3$O$_7$, even with a ratio of 4, is that the large [Fe(OH)$_4$]$^{x-}$ complex ions will have a much lower diffusion rate due to Graham's law, and so in a diluted solution their relative concentration needs to be increased to have enough collisions to react and form BaM [89]. Some of the unreacted Ba$^{2+}$ always reacted with air during the synthesis to form BaCO$_3$. Ba$_3$Fe$_3$O$_{17}$ has also been reported as a product in the hydrothermal reaction of $\gamma$-Fe$_2$O$_3$ and Ba(OH)$_2$ in an alkaline solution to make BaM, in certain molar ratios [163].

Mössbauer spectroscopy can be an excellent tool for detecting poorly magnetic phases such as $\alpha$-Fe$_2$O$_3$, $\alpha$-FeOOH, BaFe$_2$O$_4$, and structurally similar phases such as Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$. This technique was applied to study the hydrothermal synthesis of BaM from $\alpha$-FeOOH and Ba(OH)$_2$ in a ratio of Fe:Ba = 2.4. Only $\alpha$-FeOOH was present after 260 °C/24 h, but this began to transform to $\alpha$-Fe$_2$O$_3$ at 280 °C, and after 280 °C/20 h or 300 °C/10 h it was a mixture of $\alpha$-Fe$_2$O$_3$ and BaM. The optimum temperature for BaM was found to be 315 °C/20 h, which gave BaM hexagonal single crystals with a perfect TEM electron diffraction pattern, measuring 1 x 0.1 μm [164].

### 5.1.5. Other synthesis methods for BaM

When BaM was synthesised by the citrate route, from a 10 nm stoichiometric amorphous precursor decomposed at 420–470 °C, this appeared to form BaM as the sole crystalline product after 550 °C, giving a single phase XRD pattern at 700 °C and with a grain size of only 60 nm [85]. Mössbauer studies suggested that the non-magnetic BaFe$_2$O$_4$ may be present and that some cations had not diffused fully into the lattice at this temperature, but by 800 °C the Mössbauer data agreed with XRD that the pure M phase had formed, and the grain size was still below 100 nm [84]. When a sample of the amorphous precursor decomposed at 425 °C was left standing for 1 year at room temperature it had become a metastable $\gamma$-Fe$_2$O$_3$, which has been seen as an important species for the formation of BaM in other precipitation-based techniques. Upon standing for another 6 months the material had transformed to a near-hexagonal structure with physical and magnetic characteristics between those of BaM and $\gamma$-Fe$_2$O$_3$, but as the temperature was too low for a solid state reaction to occur it was assumed to have been an ionic rearrangement [165]. There are many conflicting reports regarding the ideal Fe:Ba and citrate:metals ratios for citrate routes. Li et al. reported that the optimum ratios for BaM formation from a citrate route were a stoichiometric Fe:Ba of 12, and citric acid: iron(III) nitrate of 3 (solution pH = 9), which decomposed at 208 °C, began to form BaM at 750 °C, and formed single phase BaM at 800 °C/3 h with good magnetic properties [166]. A thorough investigation into the effect of pH and citric acid:metals ratio for the synthesis of BaM reported that $\gamma$-Fe$_2$O$_3$ and BaCO$_3$ were always seen as combustion products, occasionally with $\alpha$-Fe$_2$O$_3$ as well, but never BaM. Complete complexing of citrate with iron was achieved with pH >3, and with barium as well a pH >7, and a citrate:metals ratio of 1.5 was ideal. The best product was obtained [167] with a citrate ratio of 1.5, pH of 9, and calcined at 800 °C/4 h. Huang et al. reports that the ideal ratio of Fe:Ba is 11.5 and citrate:metals of 2:1 at a pH of 7 [168]. In the author's personal experience, stoichiometric metals and a citrate:metals ratio of 1.5 is sufficient.

A variation on the standard solid state synthesis is the so-called “solvent-free” method, in which a mixture of barium and iron nitrates, cetyltrimethylammonium bromide (CTAB) and ammonium carbonate are ground together at room temperature to make a viscous solid. When this was dried at 120 °C, then precalcined at 400 °C, it formed BaM at 950 °C, although impurities of $\alpha$-Fe$_2$O$_3$ and Ba-Fe$_2$O$_4$ were seen even at the reported optimum Fe:Ba ratio of 11 [169]. The CTAB-route BaM formed highly crystalline thin, hexagonal plates ~1 μm diameter at this relatively low temperature. Microwave induced combustion was carried out on a solution of stoichiometric barium and iron nitrates (oxidising agents) and urea (CO(NH$_2$)$_2$, the reducing agent), where the urea was in ratio of Fe:urea of 12:31. In 15 min the solution had dried, dehydrated and decomposed, producing N$_2$, NH$_3$ and HNCO gasses, after which it spontaneously combusted to a temperature over 1000 °C. The as synthesised
powder was mostly BaM with some a-Fe₂O₃, but on annealing to 850 °C pure, well crystallised BaM resulted, with a particle size of only 35 nm [170].

Carbon Combustion Synthesis of Oxides (CCSO) was recently used to make BaM, by adding up to 30 wt.% of 5 nm carbon NPs (80 m² g⁻¹) with iron oxide and BaCO₃, both reactants having particles sizes of ~50 nm [104]. After drying and mixing, the reactant were fed a flow of pure O₂ at 10 l min⁻¹, and the combustion initiated by an electrically heated coil. With 5 wt.% carbon the propagation was unstable, and the front extinguished after 5 mm, but with 6.5–30 wt.% the propagation was stable throughout the reactants, generating maximum temperatures of 900–1200 °C. With under 5 wt.% no combustion occurred, and the reaction temperature and resulting particle size increased with increasing carbon content (Fig. 21a). The progress of reaction temperature with time is shown in Fig. 21b for carbon levels of 8, 10 and 12 wt.%, and the reaction lasted for about 180 s, proceeding at a slow velocity of 1.3 mm s⁻¹ with 12 wt.% carbon. The oxygen flow rate also affects propagation as it transports both oxidiser and heat to the reaction zone, and the minimum needed for complete conversion to BaM was 5 min⁻¹ (Fig. 21c), with an increasing flow increasing the reaction temperature up to 12 l min⁻¹. The activation energy for this was 98 kJ mol⁻¹ with 11 wt.% carbon, a low value leading the authors to suggest that Fe₂O₃ and BaCO₃ may catalyse carbon combustion – the only effluent gasses were CO₂ and O₂, and the BaM only contained 0.1% C. with 8 wt.% carbon the end product was mostly BaM with a degree of amorphous material, but with 11% the as-synthesised product was pure phase BaM, as a friable and spongy mass with a porosity of 70%. This consisted of 50–100 nm rectangular/irregular particles (Fig. 21d), with a mean diameter of 60 nm, and a surface area of 22 m² g⁻¹.

Hollow spheres of BaM were made by spraying an aerosol of a solution of salts into a heated zone for only one second, to give 90 nm spheres with a wall thickness of only 30 nm and a hollow centre.

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**Fig. 21.** Details of the carbon combustion synthesis of BaM. (a) Influence of 5 nm carbon NP concentration on maximum reaction temperature achieved. (b) Temperature evolution with time during the reaction with 8, 10 and 12 wt.% carbon. (c) Effect of pure oxygen flow rate on the progress of combustion with 10 wt.% carbon. (d) TEM image of pure BaM nanopowder made with 10 wt.% carbon [104].
When made at 527 °C the spheres were mainly amorphous with some iron oxide and barium nitride (an N₂ gas jet was used), and although this became fully crystalline after annealing at 727 °C, it was not BaM. When the spheres were produced at 1027 °C the product was a fully crystalline mixture of oxides, nitrides and BaM, and this formed pure BaM upon annealing at 727 °C/3 h [106]. The electrophoretic deposition of BaM has also been developed, using the careful control of a surfactant to stabilised a suspension of BaM NPs, which can then be deposited as a thick film when an electric field is applied [171].

![Phase diagram of the SrO·Fe₂O₃ system for >33% Fe₂O₃. Bottom: close up view of the region which contains the hexaferrites, derived by Langhof et al. [176]. SrM = 85.7 mol%.

Fig. 22. Top:Phase diagram of the SrO·Fe₂O₃ system for >33% Fe₂O₃. Bottom: close up view of the region which contains the hexaferrites, derived by Langhof et al. [176]. SrM = 85.7 mol%.

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5.2. Other M ferrites

The SrO–Fe₂O₃ system resembles that of barium, with again a very narrow compositional range in which the M phase can exist [172], but the Fe⁴⁺ ion is found more frequently in the strontium systems [173]. SrFe₂X has been seen as a minor product at 1420 °C after 2 h, but both this and the remaining SrM decomposed to SrFe₂W at 1435 °C which then melted at 1465 °C [174]. SrM was reported to be made from a stoichiometric mix of oxides by the standard ceramic route at 1000 °C/12 h, and sintered at 1300 °C/12 h [175]. A detailed study of the region around the SrO–6Fe₂O₃ system was made by Langhof et al. in 2009, and a phase diagram produced (Fig. 22) [176]. They found no evidence of a phase width in the composition of SrM, with the pure M phase forming only within a very narrow window of 85.71 mol% Fe₂O₃ ± 0.2%. With excess Fe₂O₃ at 87% (Fe: Sr = 6.69), α-Fe₂O₃ was a second phase after heating at 1200 °C/24 h. With excess SrO, only pure SrM was identified by XRD down to 85.0% Fe₂O₃ (Fe: Sr = 5.67), but with 84% Fe₂O₃ a second phase of Sr₄Fe₆O₁₃ was observed when heated at 1200 °C/24 h – when pure, this impurity melts at 1250 °C. The lattice parameters of SrM were c = 23.0511 Å and a = 5.8847 Å. They also found that SrM melts and forms Sr₂Fe₂X at 1418 °C, which melts in turn to form SrFe₂W at 1435 °C, and this melts to produce Fe₃O₄ at 1452 °C. Pure SrM reaches a peak density at 1350 °C, but with 84% Fe₂O₃ the lower melting SrFe₂O₄ phase forms a liquid phase in the SrM at 1206 °C, exhibiting significant shrinkage at 1210 °C, and no increase in density after 1200 °C/4 h. The Fe-rich sample with 87% Fe₂O₃ showed maximum shrinkage at 1350 °C, at which point it underwent a solid state transformation to form SrM and Sr₂Fe₂X.

An investigation of the synthesis of SrM from coprecipitated salts fired at 800–1100 °C showed that the M phase only forms as a pure product in a non-stoichiometric mixture, with an Fe:Sr ratio no more than 9, the best product requiring a ratio of 8 [53], which is lower than required to form BaM. It has also been found that stoichiometric mixtures of standard ceramic powders never fully sinter, whereas with a ratio of 11 the material is fully sintered by 1150 °C, and this is attributed to increased diffusion rates in the non-stoichiometric mixes due to induced lattice defects [143]. However, when made from a sol–gel precursor with a stoichiometric composition, the M phase was obtained mixed with a small amount of α-Fe₂O₃ between 800 and 1000 °C, and the single phase material fired to 1200 °C had magnetic properties comparable to those found in standard ceramic materials [80]. Pullar et al. reported the synthesis of SrM from a stoichiometric aqueous sol–gel precursor at temperatures as low as 700 °C [72,156]. In a citrate sol–gel process, γ-Fe₂O₃ was first observed at 500 °C, and then along with both α-Fe₂O₃ and SrM which were also detected at 600 °C, before pure SrM became the sole phase at 800 °C [177]. Another strontium-iron phase was found when, after SrM was treated with nitrogen and hydrogen atmospheres, it decomposed to form iron oxides and Sr₇Fe₁₀O₂₂ [178]. SrM was synthesised by the citrate route, and the amorphous precursor began to crystallise as SrM at the very low temperature of 550 °C with a grain size of only 42 nm, and had formed the pure M ferrite at 800 °C with grains of only 116 nm. The material had a relatively high surface area of 10.12 m² g⁻¹ indicating it was poorly sintered, and this is a typical feature of this method of synthesis [85]. Citrate sol–gel derived single phase crystalline SrM was obtained from a stoichiometric precursor at a temperature of only 250 °C, when fired in an oxygen atmosphere [179]. As has been discussed above, when made from an aqueous sol–gel process, pure SrM formed directly from α-Fe₂O₃ at 700 °C with no other intermediate ferrite precursors [139].

It was reported that hydrothermal synthesis of a stoichiometric slurry of Fe(OH)₃ and Sr(OH)₂ at 250 °C formed a mixture of SrM and α-Fe₂O₃ [159]. Hydrothermal synthesis of SrM by coprecipitation in an autoclave at 130 °C formed a mixture of α-Fe₂O₃, α-Fe₆O₁₇, SrFeO₂.₅, from which SrM began to crystallise at 750 °C and was single phase at 800 °C [180]. Atae et al. published a study of the effects of OH⁻ : NO₃⁻ ratio, hydrothermal synthesis time and temperature on the composition and magnetic properties of SrM [181]. However, whether accidentally or not, they omitted the most important information of the stoichiometry of their M ferrite precursor. They still published some useful details: with a OH⁻ : No₃⁻ ratio of 2, SrM began to form after 30 min at 220 °C, and after 2 h the sample appeared to be pure SrM. When synthesised at 220 °C/5 h, a OH⁻ : NO₃⁻ ratio of 1.5 yielded mostly α-Fe₂O₃, but with ratios of 2–7 the sample was mostly SrM with some α-Fe₂O₃ always present. All ratios gave thin platy hexagonal crystals, with dimensions of ~1.8 × 0.3 μm for ratios of 2–5, a maximum size of 5.8 × 1 μm for a OH⁻ : NO₃⁻ ratio of 6, and then a smaller size of 4.5 × 0.6 μm for a ratio of 7. When
the ratio was 8 no magnetic product was produced, which indicated that above a ratio of 6 the excess OH\(^-\) has a harmful effect on the reaction, possibly due to excess sodium ions from NaOH. Increasing the synthesis temperature from 160 to 220 °C/1 h led to a continuous increase in particles size with a ratio of 2. With a Fe: Sr ratio of 8, SrM was made at 180 °C/24 h by Jean et al., although with traces of SrCO\(_3\) and α-Fe\(_2\)O\(_3\) in the as-synthesised powder [91]. For a stoichiometric mix, only 36 wt.% of the product was SrM, and with a large excess of Sr (ratio Fe: Sr = 12:5) Sr\(_3\)Fe\(_2\)(OH)\(_{12}\) was detected. For
the ratio of 8, the as-synthesised SrM consisted of very thin hexagonal crystals 1–2.5 μm × 75 nm (Fig. 23a), and TEM demonstrated that each grain consisted of several crystallites (Fig. 23b), but that these crystallites were all oriented with the c-axis perpendicular to the plane of the grain. A synthesis temperature of at least 200 °C is required to make single-crystalline grains. After firing at 500 °C there was very little change in grain size (Fig. 23c), and the sample still contained traces of SrCO₃, but after heating at 1000 °C the grains were clearly more crystalline, and although their diameter had not changed much they were now twice as thick (150 nm) and had less-sharp, more rounded hexagonal corners (Fig. 23d) [91]. The magnetic hysteresis loops of the as-synthesised and 500 °C samples are shown in Fig. 23f. FT-IR spectra were also taken of the as synthesised SrM, and compared to that of standard ceramic SrM in Fig. 23e. The bands at 447, 552, and 603 cm⁻¹ are assigned to SrM [182], and –OH bands at 3420 and 1640 are often seen from surface hydroxy groups from the atmosphere.

It has been shown that a solid solution exists between BaM and SrM, with a steady change in lattice constants, and magnetic properties with substitution [183]. PbM is less thermally stable than BaM or SrM, decomposing at 1250 °C to α-Fe₂O₃ and melting at 1315 °C [184], and no complex hexaferrites are seen due to the high vapour pressure of PbO [185]. A substitution of up to 70% of Ba with Ca was reported whilst retaining the M structure by van Uitert in 1957 [186], and he found that an addition of 2 mol% La₂O₃ or La₂O₃/Nb₂O₅ could stabilise the phase. Pure CaM stabilised by 4 mol% La₂O₃ has since been reported by Narang and Hudiara [175], formed at 1000 °C/3 h and sintered at 1180 °C/4 h from stoichiometric oxides by a standard ceramic route, as well as the series 0.96CaO₂TiFe₁₂₋ₓO₁₉₋₀.04La₂O₃ where x = 0.1–1.0. Some rare earth metals have been totally substituted for strontium to make REFe₁₂O₁₉, despite the difference in charge between Ba²⁺ and RE³⁺ [187]. An example is LaM, although it is noted to be extremely difficult to make as a single phase, requiring a very limited heating at 1000 °C. At 800 °C the grains were 90 nm wide and 49 nm thick, growing to 200 nm by 130 nm at 900 °C, but maintaining the ratio of length to thickness of 1.5 [64]. The formation of the chromium substituted M ferrites BaFe₁₀Cr₂O₁₉ and SrFe₁₀Cr₂O₁₉ proved to be possible, but proceeded by two different mechanisms. Heating 5Fe₂O₃, BaCO₃ and Cr₂O₃ together formed α-Fe₂O₃, BaFe₂O₄ and BaCr₂O₄ as precursors, but after 5 min at 1020 °C the M phase began to form. After 2 h, M ferrite was the major phase, and the barium-containing precursor phases had gone, but a small amount of α-Fe₂O₃ persisted even after 6 h at this temperature. After 1300 °C/2 h single phase BaFe₁₀Cr₂O₁₉ resulted. With SrCO₃, the precursor phases are α-Fe₂O₃, SrCrO₄ and SrFeO₃₋ₓ, and at 980 °C SrM had already begun to form. Some SrCrO₄ persisted up to 90 min at 980 °C, but after 6 h the sample was nearly all M ferrite with a trace of α-Fe₂O₃. It appeared that the M phase formed initially as pure SrM, and the chromium slowly diffused into the lattice to form SrFe₁₀Cr₂O₁₉ over several hours, via the SrFe₁₂₋ₓCrₓO₁₉ solid solution [188].

5.3. Substituted M ferrite

BaFe₁₁.₅Co₀.₅O₁₉ has been made by ion exchange, forming the impure product at 750 °C. At 800 °C the grains were 90 nm wide and 49 nm thick, growing to 200 nm by 130 nm at 900 °C, but maintaining the ratio of length to thickness of 1.5 [64]. The formation of the chromium substituted M ferrites BaFe₁₀Cr₂O₁₉ and SrFe₁₀Cr₂O₁₉ proved to be possible, but proceeded by two different mechanisms. Heating 5Fe₂O₃, BaCO₃ and Cr₂O₃ together formed α-Fe₂O₃, BaFe₂O₄ and BaCr₂O₄ as precursors, but after 5 min at 1020 °C the M phase began to form. After 2 h, M ferrite was the major phase, and the barium-containing precursor phases had gone, but a small amount of α-Fe₂O₃ persisted even after 6 h at this temperature. After 1300 °C/2 h single phase BaFe₁₀Cr₂O₁₉ resulted. With SrCO₃, the precursor phases are α-Fe₂O₃, SrCrO₄ and SrFeO₃₋ₓ, and at 980 °C SrM had already begun to form. Some SrCrO₄ persisted up to 90 min at 980 °C, but after 6 h the sample was nearly all M ferrite with a trace of α-Fe₂O₃. It appeared that the M phase formed initially as pure SrM, and the chromium slowly diffused into the lattice to form SrFe₁₀Cr₂O₁₉ over several hours, via the SrFe₁₂₋ₓCrₓO₁₉ solid solution [188].

The Al³⁺ ion can also be substituted into BaM ferrite up to BaFe₄.₂Al₁.₇₂O₁₉ [189], and a complete solid solution exists between SrM and SrAl₁₂O₁₉ [190]. When made by a citrate gel-auto combustion process (at 800 °C), a maximum substitution of BaFe₃Al₁₂O₁₉ was reported, and unusually Fe₂O₄ was seen as a precursor at 500 °C, to be replaced by α-Fe₂O₃ and M ferrite at 850 °C, probably due to the reductive nature of the combustion process [191]. Liu et al. showed that for their hydrothermal synthesis of BaFe₁₂₋ₓAl₆O₁₉, substitution with x ≥ 6 was possible, although small amounts of BaCO₃ and BaFe₂O₄ were seen for values of x > 0.9 in the as-synthesised product (suggesting that less Ba could be used) [161]. They stated that the ideal ratio of (Fe + Al):Ba was reduced to 9.5, and that the M phase did not form until 230 °C, and was not pure phase until reacted at 250 °C/4 h. As Al³⁺ substituted for Fe³⁺, they found that they could use higher levels of Fe²⁺ precursor, to the extent that for the x = 6 sample the precursor consisted solely of Fe²⁺ and Al³⁺ ions, the Fe²⁺ all converting to Fe³⁺ during synthesis. This was attributed to the fact that Al₂O₃ is also a spinel, and aided the formation of the M phase. SEM images of the as-synthesised M crystals are shown in Fig. 20c and d. When Al-substituted SrM was made across the entire substitution range, the morphology changed drastically from hexagonal platelets ~100 nm for SrM, to irregular and angular particles with up to 4 Al ions, and elongated rods.
or needles 200 nm long with substitution levels above this [191]. Of the trivalent lanthanides Ga\(^{3+}\) and La\(^{3+}\) have the highest solubility limit in BaM, and both lanthanide doped [192] and gallium doped [193] hexaferrites have been made with total substitution of iron despite the large size of the La\(^{3+}\) ion. In\(^{3+}\) and Sc\(^{3+}\) ions have only been substituted for iron up to BaIn\(_3.4\)Fe\(_{8.6}\)O\(_{19}\) [194] and BaSc\(_{1.8}\)Fe\(_{12}\)O\(_{19}\) [195].

When Pb\(_2\)Me\(_2\)Y was attempted using mixtures of two small divalent metals such as Ni\(^{2+}\)–Cu\(^{2+}\), or a trivalent and a monovalent metal such as Li\(^+\)–Yb\(^{3+}\), no Y phase was formed but two distinct M phases were formed with different cell dimensions [21]. This suggested that the M structure will tolerate a certain amount of solid solution of transition metals without collapsing, and this has been proven correct by the manufacture of a wide range of doped M ferrites, in which iron is substituted either by a Me\(^{3+}\) or a mixture of M\(^{2+}\)/M\(^{4+}\) ions, provided they have similar ionic radii to the substituted ions.

The most common substituted M ferrite is BaCo\(_x\)Ti\(_x\)Fe\(_{12-2x}\)O\(_{19}\), which has improved properties for use in magnetic recording applications. A solid solution exists between iron(III) and titanium(IV) oxides, in which Fe\(^{3+}\) is replaced by a pair of Fe\(^{2+}\) and Ti\(^{4+}\) ions, with a resulting increase in unit cell size, to form titanospinels, magnetite and maghemite [42]. Therefore, if Ti\(^{4+}\) is added with a divalent metal which can also form a solid solution with iron, such as Co\(^{2+}\), a simple substitution of Fe\(^{3+}\) can occur. The a lattice parameter, grain size, saturation magnetisation, coercivity and remanence are all decreased with increasing x, but it was found that the Ti\(^{4+}\) ion had more effect on the grain size while the Co\(^{3+}\) ion was mostly responsible for the change in magnetic properties [196]. It has been suggested that the grain size is reduced with Ti\(^{4+}\) ions by enhancement of nucleation sites [197]. The a lattice parameter is 5.89 Å, the same as for BaM, but the c-axis has been found to increase with substitution, being 23.20 Å at x = 0.8 [198], 23.21 Å at x = 1.1 and 23.23 Å at x = 1.5 [199], because the average radius of Co\(^{2+}\)/Ti\(^{4+}\) (0.627 Å) is larger than that of Fe\(^{3+}\) (0.550 Å).

For x = 1.1 when fired to 1150 °C the grains had grown to form 1 µm platelets, and these increased to 50–150 µm between 1230 and 1290 °C [199]. However, in a sample of BaCoZrM made by the citrate route the grains were only 5 µm even after heating to 1300 °C, and DGG was never observed [200]. Nickel–zinc–titanium substituted BaM was found to have a smaller grain size than BaCoTiM, consisting of 100 by 10 nm platelets at 900 °C at x = 1 [201]. It is typical of these doped BaM systems that they form even more acicular grains that usual, with a large width-to-thickness ratio. This was found to be even more pronounced in BaCoSnM, forming very flat particles with a large surface area, but the fusion between particles was reduced inhibiting grain growth [202]. When Ba(MnTi)\(_x\)Fe\(_{12-2x}\)O\(_{19}\) (x = 0.5–2) was made by a citrate combustion method, the as-prepared powders consisted of crystalline BaCO\(_3\) and γ–Fe\(_2\)O\(_3\) and no M ferrite, with the pure M phase forming at 800 °C/4 h [98].

An investigation of the BaO–TiO\(_2\)–Fe\(_2\)O\(_3\) system at 1240 °C revealed at least 12 different mixed compounds, ranging from BaTi\(_2\)O\(_3\) with 0.2 mol% Fe\(_2\)O\(_3\) to Ba\(_{12}\)Ti\(_{16}\)Fe\(_30\)O\(_{89}\), a hexagonal ferrimagnetic compound [203]. In a study of BaCoTiM coprecipitated from chloride salts the mixture formed as hexagonal platelets 50–80 nm in diameter [204]. BaCo\(_{0.6}\)Ti\(_{0.6}\)Fe\(_{10.8}\)O\(_{19}\) made from the stearic acid gel method began to crystallise at 650 °C, becoming single phase at 750 °C with very small 10–20 nm grains, growing to 100 nm at 1000 °C and 500 nm at 1150 °C [81]. When BaCo\(_x\)Ti\(_{1-x}\)Fe\(_{12-2x}\)O\(_{19}\) was produced from the glass crystallisation method it was found that TiO\(_2\) in the glass matrix acted as a nucleation agent and accelerated the crystallisation of the M phase [196]. It has been claimed that BaCo\(_{0.8}\)Ti\(_{0.8}\)Fe\(_{10.4}\)O\(_{19}\) was prepared by this method to give platelets only 7.6 nm long and 2.4 nm thick [198].

RE substituted BaM was studied by Leccabue et al., using Gd, La, Lu and Sm as the RE\(^{3+}\) ion, and balancing the charge with an accompanying Na\(^+\) ion, to make the Ba\(_{1-x}\)RE\(_{x/2}\)Na\(_{x/2}\)M series [205]. It was found that the general solubility limit for RE in the M structure was x = 0.1, determined by Mössbauer spectroscopy. At 630–730 °C α–Fe\(_2\)O\(_3\) and BaFe\(_2\)O\(_4\) were present, and at 1100 °C there was evidence of the REFeO\(_3\) perovskite as well. The pure M ferrite had formed 1300 °C for x = 0.1, although for higher values of x it appeared that α–Fe\(_2\)O\(_3\) and REFeO\(_3\) were also present. The substitution of RE/Na appeared to result in enlarged and more clearly defined hexagonal plates, even when the FeO\(_3\) phase was present at x = 0.2, which may aid in the production of oriented ceramics (Fig. 24). A similar series of results were later published by Wang et al., who appear to have doped SrM with a variety of RE ions (Sm [206], Pr [207], La [208] and Nd) at RE:Sr ratios of 1/16–1/2, while maintaining
a constant Fe:Sr ratio of 8 (i.e., not actual substitution), and a OH−:NO3− ratio of 2 for the hydrothermal synthesis at 220 °C/3 h at a pressure of 25 bar. In all cases they found that although SrM could be made with no RE ions (although usually with SrFeO3x impurity), the RE ions did not fully substitute into the M structure under synthesis conditions, and the as-synthesised powder always contained α-Fe2O3 and RE oxides, in increasing amounts as the doping level increased. The as-synthesised compounds consisted of micron-range thin hexagonal plates. Upon subsequent calcination to 1000 (Sm and Nd), 1250 (Pr) and 1300 (La) °C/2 h, the RE could be fully substituted into the SrM, shown by the absence of RE oxide in XRD patterns, but SrFeO3−x nearly always formed as well as RE replaced Sr in the M structure, due to the non-stoichiometry of the doped ferrites. The RE doped M ferrites exhibited little change in grain size even when heated to higher temperatures, indicating that they inhibit grain growth, apart from La at higher temperatures.

It would seem that a non-stoichiometric, iron-deficient ratio of Fe:(Ba/RE) favours the formation of single phase, RE-substituted M ferrites, if no Na+ counter ion is used to balance the charge. Yamamoto et al. have made a series of RE substituted SrM and BaM ceramics, with RE such as lanthanum and neodymium, made through coprecipitation methods. Some of these are iron-deficient, but others also partially substitute Fe3+ with Me2+ to maintain oxygen stoichiometry, such as the (Ba/Nd)(Fe/Co)12O19 system, of which Ba0.99Nd0.118Co0.041Fe11.86O19 sintered at 1000 °C/2 h proved to have the optimum magnetic properties [209]. This same paper suggests that in uncompensated, RE substituted BaM, a ratio of Fe:Ba of 10.5 gives the optimum magnetic properties. A ratio of Fe:(Ba/RE) of 10.5 also seems to be favoured by Stergiou et al., for example iron-deficient ferrites synthesised by coprecipitation with substituted Dy and Gd, to make Ba1−xRExFe10.5O16.75+x [210]. For Dy this was sintered at 920 °C/2 h, and for x = 0.05 the pure M phase was made, although for x = 0.1 and 0.2 it also contained 6% and 14% α-Fe2O3. With Gd it was sintered at 1000 °C/2 h, and for x = 0.1 the pure M phase was made, but for x = 0.2 it contained 4% α-Fe2O3. Substitution of Fe3+ by Me2+ without a counter-ion was also achieved, to make oxygen-deficient single crystals of BaFe10.5Me0.25O17.05 for Me = Mg, Cd,
Co, Ni and Zn, by ionic exchange in molten salts of non-magnetic β-ferrite/BaCl₂ at 750 °C. The resulting hexagonal platelets were as small as 200 nm in diameter and 20 nm thick [211].

5.4. Y ferrite

Investigations of the BaO-Fe₂O₃-CoO system showed that Y ferrite not only formed at the stoichiometric point 20% BaO–20% CoO–60% Fe₂O₃, but also over a region of compositions (2.5–45% BaO)–(5–45% CoO)–(50–69% Fe₂O₃). Y coexists with the BaFe₂O₄, spinel, W and Z phases or a mixture of these phases over this range, but to form single phase Y the mixture must be near the stoichiometric point (Fig. 16) [46].

For stoichiometric mixtures made by coprecipitation the Y phase was found to begin to form at 950 °C, as α-Fe₂O₃ vanishes and the BaM and spinel phases drop to half their maxima, giving equal proportions of M, Y and spinel phases at 970 °C. By 1000 °C the material was virtually all Y, reaching a maximum at 1100–1300 °C. After this point Y rapidly decomposes to give mostly W and some spinel. At 1300 °C Co₂Y consisted of hexagonal grains 3–10 μm wide and 0.75–2 μm thick [21]. Investigating the use of ethanol instead of water as a solvent during coprecipitation, Lisjak and Drofenik [148] used stoichiometric iron ratios for iron chloride and barium and cobalt acetate precipitated with NaOH in a 3:1 ethanol:water solution, both in air and under a flow of Ar. They found that BaCO₃ formed as a precursor at 400 °C in both the samples precipitated under air and Ar, unlike for BaM, and that if left in air the precipitate also absorbed CO₂ to form BaCO₃. α-Fe₂O₃ and BaFe₂O₄ crystallised at 600 °C, and at 680 °C the carbonate had decomposed and the CoFe₂O₄ had crystallised. At 700 °C the BaM and Co₂Y phases had formed alongside α-Fe₂O₃ and BaFe₂O₄, a very low temperature for the formation of Y ferrite, and these remained as mixed phases when calcined at 700 °C/50 h and even 800 °C/70 h, with samples from both atmospheres, although the proportion of Y ferrite increased with temperature. The sample precipitated under Ar produced the pure Y phase after being calcined at 900 °C/50 h or at 1000 °C/10 h, where as the sample precipitated in air only formed the single phase Y at 1100 °C/3 h. Once again, this shows that the Y phase cannot crystallise without the prior crystallisation of the M phase. Co₂Y made from an aqueous sol–gel process using stoichiometric halide-based precursors consisted of only crystalline α-Fe₂O₃ from 400 °C, until BaM, BaFe₂O₄ and CoFe₂O₄ replaced this at 800 °C. At 1000 °C the powder was nearly completely Co₂Y, with a trace of α-BaFe₂O₄ but no BaM [73]. Using a combustion process based of EDTA complexes, it was found that a solution pH of between 8 and 10 was best to form both a stable EDTA complex and a quality Co₂Y product. All the organics and nitrates had combusted by 700 °C, and from the precursor phases BaFe₂O₄, CoFe₂O₄ and α-Fe₂O₃, and Co₂Y began to form at 900 °C, being single phase at 1000 °C [212]. At pH values <8 some of the precursors remained in the final product.

Zn₂₃Y was made from the coprecipitation of hydroxides and barium carbonate, forming α-Fe₂O₃ at 350 °C, BaFe₂O₄ at 780 °C and Zn₂Y at 1100 °C. This did not become the single phase material until 1200 °C with a grain size of 2 μm, and it decomposed at 1250 °C into ZnFe₂O₄, α-Fe₂O₃ and BaO [213]. In a study of the effects of cation deficiency on the formation of the Y phase, it was seen that for Ba₂Zn₀.₅Co₀.₅Cu₀.₅Fe₁₂₋ₓSnₓO₃₋₀.₅-x the pure Y phase could form for values up to x = 1, and that for x = 1.5 other phases were present as well, mainly BaFe₂O₄. This indicates an iron-non-stoichiometry limit for the Y structure of around Ba₂Me₂Fe₁₁O₁₇.₅ [214]. The deficiencies caused ion vacancies which promote mass transfer and the sintering process, thus increasing the density of the deficient ferrites compared to the pure Y at equivalent temperatures (e.g., 4.44 g cm⁻³ for x = 0 and 5.01 g cm⁻³ for x = 0.5 at 975 °C). This also lead to DGG occurring in the deficient ferrites above 950 °C, trapping pores inside and creating grains hundreds of microns in length.

Using Ba²⁺ as the large cation, pure Ni₂Y, Zn₂Y and Mg₂Y have all been made successfully [7], and Cu₂Y was also produced, although only as a mixed phase with BaM ferrite [21]. Sudakar et al. formed Ni₂Y from a thermal gel-crystallisation process that crystallised as a mixture of Y, spinel, α-Fe₂O₃ and BaFe₂O₄ phases (grain size <100 nm) directly from a stoichiometric precursor at 750 °C, and had formed the single Y phase at 950 °C [25]. When Zn₂Y was made from a citrate combustion process, it was found that the citrate mass was lost between 180 and 220 °C, with a combustion temperature of 235 °C, and residual carbon was lost between 300 and 440 °C. At 850 °C γ-Fe₂O₃, BaFe₂O₄ and BaM were present along with Y, while at 950 °C the powder appeared to pure Zn₂Y from XRD. However,
magnetic measurements showed that this still contained small amounts of magnetic phases such as γ-Fe$_2$O$_3$ and BaM, but these could be prevented by thermal treatment at 650 °C before calcination at 950 °C to remove any residual carbon, resulting in a magnetically softer Y ferrite [215]. In a study of Ba–Sr and Ni–Co solid state interdiffusion in the Ba$_{2-x}$Sr$_x$Co$_2$$_y$Ni$_{3-y}$Y system at 1200 °C, it was found that a maximum for the Ba–Sr interdiffusion coefficient existed at $x = 1.4–1.5$, and a maximum for the Co–Ni interdiffusion coefficient existed at $y = 1.0$, when $x$ and $y$ were varied individually. The Ba–Sr interdiffusion coefficient was several times larger with $y = 0$ (Co$_2$Y) and than when $y = 2$ (Ni$_2$Y), and if both $x$ and $y$ were varied simultaneously, both the Ba–Sr and Co–Ni interdiffusion coefficients varied exponentially with $y$ (Ni content) [216]. Mg$_2$Y, which is now known to be a MF ferrite, was made by a citric acid combustion process, dried and self combusted at only 120 °C. When calcined at 1080 °C/5 h the powders consisted of mostly Mg$_2$Y, with some BaFe$_2$O$_4$ and MgFe$_2$O$_4$, and at 1170 °C the only impurity was <2 wt.% MgFe$_2$O$_4$. Unlike in Zn$_2$Y, where the Zn$^{2+}$ ions occupy only tetrahedral positions, in Mg$_2$Y these authors found that Mg$^{2+}$ was distributed throughout the cation positions [217].

Castelliz et al. found in 1969 that Co$_2$Y and Ni$_2$Y phases formed with up to 80% substitution of barium by strontium [21], and Perekalina et al. reported in 1970 [230] that fully substituted Sr$_2$Zn$_2$Y existed, albeit with a distorted lattice. Castelliz et al. also reported that when the Pb$^{2+}$ ion was used as the large cation, the Y structure was never formed for stoichiometric Y mixes, forming the W phase instead. This W phase was pure for Cobalt and Zinc, but it was also mixed with the PbM phase for Nickel, Copper and Manganese, and a similar lack of any Y phase was found with the smaller Sr$^{2+}$ cation. However, the Co$_2$Y and Ni$_2$Y phases did form with up to 50% substitution of Barium by lead, with the X phase also present as a small impurity in the nickel series. Therefore, the Y phase can only tolerate up to 50 mol% lead substitution of barium. In the pure Pb$_2$Co$_2$Y mixtures DGG had already begun at only 1100 °C/3 h, with grains over 100 μm in diameter, and grain growth inhibitors or variations in the heating cycle seemed to make little difference. This excessive growth of the PbM phase was attributed to its persistence, as the homogeneous mixture of oxides separates into fractions of differing compositions, eventually forming W and X. The T block in Y ferrites requires the diffusion of a second lead atom through the oxygen layers, but due to their low surface area diffusion of the large lead atoms will be very slow. The structure of W and X resemble M more than Y, Z or U which all contain the T block, so these phases are formed preferentially. The large M plates also had amorphous MeO and PbO at their grain boundaries resulting in a deficiency of these in the structure, and possibly a solid solution of M$^{2+}$ in PbM ferrite, changing the lattice parameters [21].

5.5. Z ferrite

Z ferrites are difficult compounds to form. A temperature of at least 1200 °C is required, the Z phase usually coexisting with some or all of the phases M, Y, W and spinel. It has been reported that 1225 °C appears to be the optimum temperature, but the Z phase was only obtained as a major component mixed with the W phase [218]. Single phase Z is notoriously hard to produce. However, in the phase diagram (Fig. 16) Z extends over a wider range of compositions than Y ferrite, forming the regions Y + Z, Z + BaFe$_2$O$_4$, M + Z, M + Z + W, Z + W, Y + Z + W, and pure Z near the stoichiometric region 17.65% BaO–11.73% CoO–70.60% Fe$_2$O$_3$ [46]. This may be because, unlike Y ferrite, the structure of Z is related to both Y and M, and therefore all the hexagonal ferrites.

In experiments comparing the formation of Z from both salts and oxides, it was found that Z is never formed directly, and must result from the topotactic reaction of the two previously formed M and Y stages, irrespective of the starting materials [219]. With salt precursors the Z phase starts to form at 1100 °C, and at 1200 °C the M and Y phases begin to decrease rapidly as the Z phase increases, to form a maximum of 90 mol% Z at 1260 °C/2 h. Any longer at this temperature, or an increase in this temperature, and the Z phase decomposes to the W phase. With oxides, the Z phase formed at the same temperature, but the W phase forms simultaneously causing the Z phase to decompose as it is being made, and resulting in a maximum yield of only 62 mol% Z. Assuming that the rate limiting step is diffusion driven and the reaction occurs at the interface between the hexagonal faces, it was suggested that two simultaneous stages must coexist, one decisive at low temperatures, one at high temperatures. At 1100–1200 °C Z product accumulation between the M and Y reagent surfaces could
restrict the surface diffusion, and at temperatures over this the rate limiting step could be a topotactic reaction at the M/Y interface [219]. The kinetics of this reaction have not so far been elucidated.

Above certain temperatures it is evident that some grains grow at an enormous rate relative to the others, giving a material containing a wide range of grain sizes, and this seems concurrent with formation of the Z phase at 1250 °C, resulting in the large platy grain morphology. This growth is much greater in the direction of the hexagonal plane, perpendicular to the c-axis [220]. The grain size becomes even more exaggerated by DGG after 1260 °C/10 h, 1290 °C/10 h or 1300 °C/10 min, giving huge plates tens or even hundreds of µm in diameter but still only a few µm thick, and with a corresponding loss of density in the final product, probably as pores are enclosed within the grains [221]. No DGG was seen after heating a stoichiometric Co₂Z mixture at 1220 °C for 24 h, but it had not formed the single Z phase.

The decrease observed in bulk density accompanying this grain growth could be explained by surface diffusion, but the rate of growth of individual grains was too great to be explained by solid state diffusion alone. Electron microscopy showed the plates contained elevated layers (Figs. 18 and 25), a typical feature of growth from vapour or melting. No evidence was seen for melting, but there were signs of vaporisation/condensation and supersaturation mechanisms, as well as of solid state diffusion. Some regions of higher energy on the surface, the result of dislocations, inhomogeneity or defects, form points where material would be expected to escape as a vapour phase, which then condenses on regions of lower energy as stacks of a spiral or circular shape, and this was also observed on the interior in Co₂Y grains. On the exterior of the Co₂Z grains there were clear stacks of hexagonal plates, and this is typical of slower growth from a lower degree of vapour supersaturation, as would be expected for the outside of the grain. All the laminas were roughly the same thickness, of 0.1–0.5 µm, and the same features were observed in Co₂Y particles heated to 1250 °C [48].

When prefired Co₂Z samples were sintered in a magnetic field to produce oriented samples, the oriented particles were observed to grow at the expense of the unaligned grains. This resulted in an oriented product, but the grains were no larger than in randomly aligned samples fired without an external field. Some large grains 10–20 µm in diameter appeared after 1260 °C/24 h, and DGG occurred at temperatures over 1290 °C [221]. The transport mechanism was suggested as being a mixture of grain boundary and volume diffusion, but porosity data indicated that the densification mechanism was via pore removal through a volume driven lattice diffusion process. The oriented samples were more sintered, with a density of 97% achieved [221]. It has been reported that if the stoichiometric Co₂Z phase precursor formed at 1080 °C by normal ceramic routes, consisting of a mixture of BaM, Co₂Y and CoFe₂O₄, was then wet milled in water for 1 h and subsequently calcined at 1230 °C/2 h, a more pure Z phase was obtained, but this was still only 71% Z ferrite from XRD data. However, when half of the barium was substituted by strontium to make Ba₁.₃Sr₁.₅Co₂Z, this increased to 91% Z phase, suggesting that the strontium substituted Z phase may have more favourable thermodynamics [222].
There have been several papers on the formation of Z ferrites from coprecipitation methods, typically using stoichiometric amounts of precursor, unlike for the formation of M ferrites. Hsiang and Yao reported that BaM and Co₂Y formed directly from BaCO₃ and amorphous Fe₂O₃ when coprecipitating Co₂Z from stoichiometric nitrates, with no crystalline α-Fe₂O₃ or BaFe₂O₄ precursors detected, unlike in other Z ferrite synthesis routes [223]. The only crystalline phase seen in the as-precipitated powder was BaCO₃. This BaCO₃ decomposed to BaM at 700 °C, and Co₂Y formed between 700 and 850 °C, a low temperature for Y ferrite, and apparently without crystallisation of the intermediate CoFe₂O₄ spinel phase, which is normally seen as a precursor to Co₂Y. At 900 °C the powder consisted of a mix of BaM and Co₂Y, but at 1100 °C only Co₂Y was observed in the XRD pattern. Clearly this cannot stoichiometrically be pure Co₂Y, but a similar Co₂Y-only precursor to Z formation (by a standard ceramic route) was reported by other authors at 1200 °C, the XRD patterns showing a majority Co₂Z phase (with some Co₂Y) at 1250 °C [32]. Hsiang and Yao show that this single Co₂Y precursor phase contained a large number of twinned grains in TEM images, and they suggest that the BaM diffused into the Co₂Y lattice structure, the stresses causing twinning, prior to Co₂Z formation [223]. The Co₂Z phase began to form at a temperature of 1150 °C, and the single Z phase was present at 1200 °C, as thick hexagonal grains up to 10 μm wide and several μm high. This is a reasonably low temperature for single phase Co₂Z to form, reflecting the intimate mixing of the precursors in the coprecipitation process. Other workers have also shown that high quality Co₂Z with good magnetic properties can be made at 1200 °C via a citrate combustion process, and again with the BaM phase disappearing before the crystallisation of the Z phase, as shown in Fig. 26 [102].

When Co₂Z was made from a stoichiometric aqueous halide-based sol–gel process, it had formed α-Fe₂O₃ at 400 °C, and at 800 °C it had been replaced by BaM and CoFe₂O₄, but there was no observed BaFe₂O₄, unlike in the Co₂Y made by the same process. This was suggested to possibly be due to the higher percentage of barium present in Co₂Y (Fe:Ba = 6 for Y, 8 for Z). At 1000 °C the CoFe₂O₄ had been replaced by Co₂Y, which as always coexisted with BaM in equal proportion prior to Co₂Z formation. The M and Y phases persisted to over 1100 °C, but as Co₂Z began to form at 1200 °C the loss of BaM was much more apparent that of Co₂Y, and only the Y phase remained as a major secondary phase until seemingly pure Co₂Z was formed at 1250 °C [75]. This has also been reported previously, but it remains unclear why the two precursor hexaferrites should not decrease at the same rate if the formation process is indeed a topotactic reaction between the two phases. As usual, the Co₂Z crystallisation occurred along with DGG to form very wide hexagonal plates (Fig. 25), and the Z phase was stable with no decomposition to Co₂W up to 1300 °C, although there was even more DGG at these higher temperatures. As with the M ferrites made by the same sol–gel process, the precursor powder retained the halides until reasonably high temperatures, loosing 8% total weight between 400 and 1000 °C, as the weight% of chlorine decreased from 5.4 wt.% to 0.1 wt.%, and bromine from 5.9 wt.% to 0.03 wt.% [155]. Once again the halides, and in particular chlorine, seemed to have a retardation effect on the formation of BaM, and in this case also on CoFe₂O₄, which did not form until a relatively
When made from a citrate based process, the Z phase never forms directly from combustion of the citrates, as is sometime seen with M ferrites. When a stoichiometric citric acid:Co 2Z precursor was dried at 135 °C/10 h and heated, combustion occurred around 210 °C, and all hydrocarbons were combusted by 350 °C. When heated to 600 °C α-Fe 2O 3 and BaFe 2O 4 had crystallised, to be replaced by BaM and CoFe 2O 4 at 800 °C, and the spinel was replaced by Co 2Y at 1000 °C. At 1100 °C the formation of Co 2Z coincided with the loss of BaM but not Co 2Y, as observed in some coprecipitation reactions as well, and discussed earlier. Co 2Z was very much the majority phase at 1150 °C, and was the only phase detected by XRD at 1150–1250 °C, supported by the magnetic data. The grain size of the Co 2Z plates grew from a very small 50–300 nm after 1150 °C/6 h, to 3 μm diameter after 1250 °C/6 h, still a relatively small grain size at this temperature [86]. The powder calcined at 1150 °C could also be sintered at only 1200 °C/6 h to produce a ceramic >95% dense, although DGG had occurred.

Barium can be fully substituted by strontium in the Z structure. Sr 3Zn 2Z was reported in 1970 [230], and Pure Sr 3Co 2Z was first synthesised by Pullar and Bhattacharya from an inorganic sol–gel precursor in 2001, forming the single Z phase at 1200 °C/3 h from SrM, α-Fe 2O 3 and CoFe 2O 4 precursors [224], without formation of the Y phase as an intermediate, a feature that has always been observed as a co-precursor in the formation of barium–Z ferrites. This raises questions about the topotactic nature of Sr 3Co 2Z synthesis, which have yet to be answered. Since then a series of Sr-substituted (Ba 1–xSr x) 3Co 2Z was made with x = 0–0.8, sintered at 1250 °C/4 h and with high densities of >5.1 g cm −3 [225]. Takada et al. synthesised polycrystalline Ba 1.5Sr 1.5Co 2Z and Sr 3Co 2Z from stoichiometric oxides/carbonates by solid state methods, and were sintered at 1250 and 1210 °C, with oxygen partial pressures of 101.3 and 21.3 kPa, respectively. This resulted in well sintered samples with densities 93% and 95% of the theoretical maximum, and grains formed as hexagonal plates between 5 and 10 μm diameter and 1–2 μm thick (Fig. 27). Magnetically oriented pellets sintered for 16 h achieved even higher densities of 98% and 97%, respectively [226]. A citrate route has also been used to make Sr 3Co 2Z, from precursor powders pyrolised at 400–450 °C, and then calcined at 1200 °C/5 h in air. It was found that single phase Sr 3Co 2Z had a very small thermal stability range for formation between 1195 and 1210 °C, and also contained the U phase at 1190 °C and W phase at 1220 °C [227]. In a study of Ba–Sr interdiffusion in Ba 3–xSr xCo 2Z, it was found that the interdiffusion coefficient reached a minimum at x = 1.5, and that the Z ferrites had larger Ba–Sr interdiffusion coefficients than the W or Y ferrites – two orders of magnitude larger than for W at 1200 °C. It was suggested that this was because there are four oxygen layers between the Ba/Sr ions in the Z ferrite c-axis, but 6 layers in W ferrite. The interdiffusion zones between SrCo 2W and BaCo 2W were 80 and 800 μm, after annealing at 1150 and 1200 °C/24 h, respectively, while between Sr 3Co 2Z and Ba 3Co 2Z they were much larger at 560 and 3100 μm, after annealing at 1150 and 1200 °C/24 h, respectively [228].
The Z phase is sensitive to barium substitution with lead in a similar manner to Y, only able to withstand up to 17 mol% substitution [21]. The Z structure can also only withstand a substitution of Ba$^{2+}$ by La$^{3+}$ up to = 13 mol%, with a decreasing cell length with substitution [229], but it is much more tolerant of substitution with strontium up to 100% [230]. Zn$_x$Co$_{2-x}$Z was made for $x = 0.4, 0.8, 1.2, 1.6$ and $2$ by a citrate sol–gel process, and formed the single phase Z ferrite at 1200 °C for all mixtures, with little change in magnetic permeability [231]. When Ni$_2$Z was formed from a thermal gel-crystallisation process, it crystallised as a mixture of Z, spinel, $\alpha$-Fe$_2$O$_3$ and BaFe$_2$O$_4$ phases (grain size <100 nm) directly from a stoichiometric precursor at 750 °C, and had formed the single Z phase at 950 °C [25].

5.6. W ferrite

The W phase forms over a wide range of compositions to form the mixed phases W + CoFe$_2$O$_4$, W + CoFe$_2$O$_4$ + $\alpha$-Fe$_2$O$_3$, W + M, W + Z, W + M + Z, W + Z + Y, W + CoFe$_2$O$_4$ + Y, and single phase Co$_2$W around 9.1% BaO–18.2% CoO–72.7% Fe$_2$O$_3$ [46]. It is the most iron rich of the hexagonal ferrites to contain a small divalent ion, requiring a higher temperature to form than the other common hexagonal phases, and it is often formed as a decomposition product of these. When made by standard ceramic techniques from stoichiometric mixtures of oxides and barium carbonate, Co$_2$W does not begin to form until 1200 °C, as a mixed phase with BaM and the spinel ferrite, and forms the pure compound over a narrow range from 1250 to 1300 °C, at which point DGG has begun and the grains grow to 60 µm. Over this temperature it begins to decompose to mixtures of W, BaM and spinel again, resulting in grains 90 µm in diameter containing traces of BaFe$_2$O$_4$ over 1350 °C, and finally fusing at 1440 °C. The ferrite material contains 7% FeO at 1400 °C, and the lattice parameter of the decomposition spinel is between those of magnetite and cobalt spinel indicating that a solid solution of the two has formed, and this reduction may be a driving force for the decomposition [232].

Lisjak et al. compared the direct synthesis from oxides and the two step synthesis from previously synthesised M and S phases for the synthesis of BaNiZnFe$_{16}$O$_{27}$ by co-precipitation [233]. When made directly in one step, the amorphous co-precipitate formed spinel and M phases as expected, which reacted to form the W phase between 1200 and 1300 °C/3 h. However, even at the higher temperature, some spinel phase remained. With the two-step synthesis, two separate BaM and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ solutions were co-precipitated. The spinel co-precipitate showed poorly crystalline spinel phase already in the as-synthesised powder, whereas the amorphous BaM co-precipitate crystallised to BaM at 700 °C. When these two separate phases were reacted the W phase did not form until a higher temperature of 1250 °C, but after 1250 or 1300 °C/3 h the pure W phase had formed. Therefore, at the very least a longer calcination time or higher temperature would be need for the single step synthesis to form the pure W phase. These authors calculated that for the single step synthesis, the probability of making pure W was 0.4, lower than that of making multiphase powders, whereas for the two-step synthesis the probability of making a single phase was 0.67, higher than that of forming a multiphase product.

Naiden et al. investigated the formation of BaCo$_{0.7}$Zn$_{1.3}$W by XRD. They made diagrams of composition evolution with sintering temperature for synthesis by a standard ceramic route (Fig. 28a), and from ultradispersed oxide precursors (UDPs) with stated a particle size of 0.85 nm (no evidence is
given for a such a tiny particle size, and I imagine that it is an error, and should be μm), made by mechanochemical activation from high energy ball milling for 20 min with a very high weight ratio of balls:powder of 20 (Fig. 28b) [49]. As can be seen, the standard ceramic route consisted of mixtures of Y, M, spinel (S) and a small amount of BaFe₂O₄ at 1000 and 1100 °C, with the amount of S increasing as Y decreased. The W phase began to form at 1150 °C, and rapidly became the major phase above 1200 °C, with the maximum W content of nearly 100% forming at 1300 °C, and no significant decomposition at 1350 °C. By comparison, after sintering at 1000 °C/6 h, the UDP powder was still mostly the UDP precursor, with small amounts of S and M, and no Y phase. The UDP precursor began to decompose at 1150 °C, when a trace of Z formed, and the M and S phases disappeared as the W phase formed rapidly, being the major phase at 1200 °C (~65%), but again peaking at 1300–1350 °C. Therefore, the UDP precursor began to form W at a lower temperature, but still required standard ceramic temperatures to completely form the W phase.

Co₂W made from a stoichiometric aqueous sol–gel precursor formed α-Fe₂O₄ at 400 °C, and at 800 °C was replaced by CoFe₂O₄ and BaM, which persisted as the sole phases up to 1150 °C, until single phase Co₂W was formed at 1200 °C. No BaFe₂O₄, Co₂Y or Co₂Z were observed as intermediate phases, and Co₂W remained as the sole phase up to 1300 °C, with no apparent decomposition [74]. The rapid conversion of BaM and CoFe₂O₄ to Co₂W occurred along with DGG forming grain tens of microns wide, and this was even more extreme at 1300 °C.

Ni₂W formed from a thermal gel-crystallisation process crystallised as a mixture of Y, spinel and α-Fe₂O₃ phases (grain size <100 nm) from a stoichiometric precursor at 750 °C, and formed the single W phase at 950 °C [25]. Like BaM ferrite, the W phase can withstand total replacement of barium with strontium or lead, implying it is the T block which is sensitive to barium replacement, as shown in the Y and Z ferrites [21]. Ba₀.₉La₀.₀₅Na₀.₀₅Zn₂W showed the BaM, α-Fe₂O₃ and LaFeO₃ precursors, but the La-substituted M ferrite did not appear as a precursor to the W phase, which was pure at 1300 °C. At 1400 °C it had decomposed into X ferrite and a second unidentified magnetic phase, observed by Mössbauer spectroscopy [205].

Langhof et al. found that SrFe₂W formed between 1350 and 1440 °C, decomposing above this temperature into Fe₂O₄, and it had lattice parameters of a = 5.8969 Å and c = 32.799 Å [176]. SrZn₂W is the most important W ferrite for its magnetic and microwave properties, usually when doped with another divalent metal ion, and forms at a low temperature of 1100 °C [234]. The addition of sodium to SrZn₂W had the effect of lowering the grain size dramatically to only 0.5–1.5 μm at 1225 °C, increasing to 1.8–4.0 μm after 1300 °C for only 30 min, and after 2 h at this temperature the grains had undergone DGG to become 3–60 μm in diameter [235]. In a study of Ba–Sr and Ni–Co solid state interdiffusion in the BaₓSr₁₋ₓCo₂₋ₓNiₓW system at 1250 °C, it was found that a minimum for the Ba–Sr interdiffusion coefficient existed at x = 1.0–1.2, and a minimum for the Co–Ni interdiffusion coefficient existed at y = 0.8–1.1, when x and y were varied individually [236]. This was the opposite trend to that seen by the same authors in the Y ferrites (two maxima), and was attributed to the existence of the R block in the W ferrites, which is not present in the Y ferrites.

5.7. X ferrite

The X ferrites are usually seen mixed with M and W phases, and are extremely hard to separate. Fe₂X was the first X ferrite to be produced as a pure single crystal sample only after 70 attempts, and even then a section of BaM phase had to be ground out of the crystal [8]. Pure single crystal Co₂X has also been grown from a flux [19], as has Zn₂X [20] and Cu₂X [237]. Polycrystalline Fe₂X has been made from the coprecipitation of oxalates, the X phase forming at 950 °C and becoming pure phase between 1000 and 1200 °C. Beyond this temperature it decomposed to BaM and α-Fe₂O₃, the Fe²⁺ making the compound unstable at elevated temperatures [238]. Recently Co₂X, Ni₂X and Cu₂X have all been made from stoichiometric oxides at 1250 °C/5 h [239]. Despite this, Gu reported making a series of X ferrites by standard ceramics routes from stoichiometric oxides, including Fe₂X, Co₂X, Ni₂X, Zn₂X, Cu₂X, Mn₂X and Mg₂X, all sintered at much higher temperatures between 1300 and 1400 °C/4 h [240]. Pullar et al. made what was presumed to be Co₂X from a stoichiometric aqueous sol–gel precursor, which exhibited at 1200 °C an XRD pattern similar to, but different from, M and W ferrites, without DGG occurring [76], but as with their Co₂W samples the only ferrite precursors
were CoFe$_2$O$_4$ and BaM at 1000 °C. The composition was confirmed by XRF to be Ba$_{1.98}$Co$_{1.85}$Fe$_{28}$O$_{45.83}$. Haijun et al. made Zn$_2$X and Co$_2$X ceramics from the citrate process which also formed the pure X phase at 1200 °C, with grains under 5 μm [241]. Sudakar et al. formed Ni$_2$X from a thermal gel-crystallisation process that crystallised as a mixture of X, spinel and α-Fe$_2$O$_3$ phases (grain size <100 nm) from a stoichiometric precursor at 750 °C, and had formed the single X phase at 950 °C [25]. Xiong and Mai made Co$_2$X NPs from a stoichiometric stearic acid sol–gel precursor, and when the gel was heated to 650 °C it contained γ-Fe$_2$O$_3$ and BaCO$_3$. However, XRD and electron diffraction from TEM showed this transformed into single phase Co$_2$X at only 750 °C, with a very small particle size of 19–23 nm, and a surface area of 49 m$^2$ g$^{-1}$ [82]. This grain size had only increased to 245 nm even upon heating to 1150 °C, and the surface of the NPs showed a highly non-stoichiometric composition. Ba$_{1.98}$La$_{0.05}$Na$_{0.05}$Zn$_2$X showed the same precursors as with W, and again the La-substituted M ferrite did not appear as a precursor to the X phase, which was not single phase until 1400 °C/6 h [205].

Sr$_2$Fe$_2$X was synthesised from stoichiometric oxides via standard solid state ceramic methods, but sintered in both air and CO$_2$ atmospheres. When sintered in air at 1300 °C it was a mixture of BaM and α-Fe$_2$O$_3$, but became the X ferrite at 1350 °C. When sintered in CO$_2$ it formed Sr$_2$Fe$_2$X at a lower temperature of 1275 °C, but became the X ferrite at 1325 °C [242].

5.8. U ferrite

These are extremely hard to make as a pure polycrystalline material, and until recently had only been seen as mixed phases with Z and Y ferrites. In 1968 Zn$_2$U single crystals were grown from a flux, and although they were mostly intermixed with Z and Y phases, some pure single crystals were identified and separated by their Curie point [23]. In 2001 Pullar et al. demonstrated the onset of Co$_2$U formation at 1000 °C, with a phase resembling, but different to, Z ferrite, and with no DGG occurring even at 1200 °C, in a marked contrast to Z ferrite formation, in ferrites made from an aqueous sol–gel process [76]. At 1000 °C the precursor resembled that of Z ferrite, with the BaM and Co$_2$Y phases present, but also with CoFe$_2$O$_4$ (not seen in their Co$_2$Z precursor at this temperature, after Co$_2$Y had formed) and an unidentified Z-like phase, that was assumed to be the onset of Co$_2$U formation. The composition was confirmed by XRF to be Ba$_{4.30}$Co$_{2.13}$Fe$_{36}$O$_{60.43}$. Lisjak et al. compared Co$_2$U made from co-precipitation and high-energy ball milling, both sintered at 1250 °C, and found that the milled powders had a density of 4.2 g cm$^{-3}$, compared to only 3.6 g cm$^{-3}$ for the co-precipitated powders [244]. Co$_3$U NPs made from a stoichiometric stearic acid sol–gel precursor were γ-Fe$_2$O$_3$ and BaCO$_3$ at 650 °C, but became single phase Co$_3$U at only 750 °C, with a very small particle size of 10–25 nm (surface area = 53 m$^2$ g$^{-1}$) [83]. As with the Co$_2$X NPs made by the same process, the surface of the NPs showed a highly non-stoichiometric composition, and grain size was only 180 nm at 1150 °C.

Fig. 29. The phase evolution with time of Co$_2$U made by (a) standard ceramic route, and (b) from ultradispersed oxide precursors (UDPs). Note that on the original diagram the x axis was mislabelled as K, not °C [49].

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Naiden et al. also investigated the formation of Co$_2$U by XRD. They made diagrams of composition evolution with sintering temperature for synthesis by a standard ceramic route (Fig. 29a), and from ultradispersed oxide precursors (UDP)s with an incredibly small stated particle size of 0.55 nm (I imagine that this is an error, and that it should be μm), made by mechanochemical activation from high energy ball milling for 20 min with a very high weight ratio of balls:powder of 20 (Fig. 29b) [49]. As can be seen, the standard ceramic route consisted of mixtures of Y, M and spinel (S) (no BaFe$_2$O$_4$), with a trace of the U phase already, at 1000 °C. At 1100 °C the U phase had begun to increase as the amount of M, Y and S decreased. The U phase content peaked (~60%) at only 1200 °C, as the M phase reached zero, and already by 1250 °C the U phase had decomposed and the Z phase formed to equal proportions of 50% each. As temperature further increased, the Z phase increased as the U phase linearly decreased, and traces of the W and X phases appeared. At 1350 °C the sample seems to consist of ~60% Z with small (<10%) amounts of U, Z and W, and the missing % content is not accounted for or identified. By comparison, after sintering at 1000 °C/6 h, the UDP powder was still mostly the UDP precursor (>80%), with 20% S. At 1100 °C a trace of the U phase had appeared, and the UDP precursor began to decompose above this temperature forming Z, X and U at 1150 °C, although the U content has already reached a maximum of around ~15%. At 1200 °C the UDP has nearly all decomposed, but to form the X phase, not U, and by 1300 °C the U phase has nearly all gone, to form ~95% Co$_2$X. This suggests that the stoichiometric Co$_2$U UDP precursor actually thermodynamically favours X ferrite formation above 1150 °C, and unexpectedly this appears to be a very successful way of producing highly pure Co$_2$X.

Lisjak et al. reported in 2004 that in standard ceramic processing, U formation occurred between 1200 and 1400 °C resulting in mixed U and Z phases, whereas pure samples of Co$_2$U, Zn$_2$U and Ni$_2$U could be made by either high-energy ball milling the reactant oxides first, or by topotactically reacting M and Y ferrites [245]. However, Ni$_2$U was crystallised from a thermal gel-crystallisation process as a mixture of U, spinel, α-Fe$_2$O$_3$ and BaFe$_2$O$_4$ phases (grain size <100 nm) from a stoichiometric precursor at 750 °C by Sudakar et al., and this formed the single U phase at only 950 °C [25]. In a recent publication Cu$_2$U, Co$_2$U, Fe$_2$U, Mn$_2$U and Mg$_2$U where all synthesised via a citrate route, and subsequently calcined twice at 1250 °C/5 h, with milling in between firings [246]. These authors found that only Cu$_2$U crystallised as a single U phase (although EDS should it to be about 25% Cu deficient, nonetheless), the other phases coexisting with very minor amounts of BaFe$_2$O$_4$ (Mn$_2$U and Fe$_2$U), or α-Fe$_2$O$_3$ and Z ferrite (Co$_2$U and Mg$_2$U). They used $^{57}$Fe NMR spectra to characterise the structure, and found that in Mn$_2$U Fe$^{3+}$ was substituted by Mn$^{3+}$ in the octahedral 4a and 12k lattice sites.

Recently Meena et al. have made several U ferrites by the standard ceramic route from stoichiometric precursors, sintered at 1250 °C/5 h. The series Ba$_4$Co$_{2-x}$Mn$_{x}$Fe$_{36}$O$_{60}$ was made in steps of $x=0.5$, and all formed the single phase U ferrite with large grain sizes between 10 and 20 μm, but without apparent DGG [247]. The density of these samples was low, ≤90% in all cases. Similarly the Ba$_4$Mn$_{2-x}$Zn$_x$Fe$_{36}$O$_{60}$ series was made by the same methods, sintered at 1300 °C/4 h, with even lower densities from 90% and 83% as $x$ increased, and grain sizes between 10 and 20 μm, but >20 μm for $x=1$ [248]. When lanthanum was substituted for barium in (Ba$_{1-x}$La$_{2x}$)$_4$Co$_2$U ($x=0.1$, 0.15 and 0.2), and sintered at 1250 °C/4 h, the pure U phase was maintained, although all lattice parameters reduced and the c:a ratio increased with increasing amounts of the smaller La$^{3+}$ ion. The density also decreased from 91.7% to 82.5% with increasing $x$, and the grain size was between 8 and 20 μm in all cases [249]. The same authors have since reported Ba$_{4}$La$_{2}$Co$_2$U ($x=0.25$, $\square= vacancy$) and $P^+$ substituted Ba$_{4}$Co$_{(1-x)P_{2x}}$U ($x=0-0.2$), all of which reportedly form the single U phase when sintered at 1250 °C/6 h, albeit with high porosity up to 19% and grains up to 20 μm [250]. This means that fully $P^+$ substituted Ba$_{4}$P$_{0.8}$Co$_{(1-0.2)}$U ($x=0.2$) was achievable.

In one of the most exciting developments in U ferrites, Sr$_4$Co$_2$U has just been characterised by Okumura et al. [34] as exhibiting a RT ME effect, similar to that seen in Sr$_4$Co$_2$Z. The ferrite was made from stoichiometric oxides precalcined at 1000 °C, and then sintered at 1250 or 1280 °C/16 h in air or oxygen, and cooled down slowly to RT over 22 h in O$_2$. Despite this laborious preparation, the authors failed to obtain a totally pure phase U ferrite, as it contained M and X ferrites as minor phases, but interestingly no Z ferrite. As shown in Fig. 12, TEM images showed the Sr$_4$Co$_2$U phase to be well defined, with none of the stacking faults observed previously in Co$_2$U (Fig. 13).
5.9. Sintering aids

Many electronic components are made as multilayered chips or surface mounted devices, such as multilayer chip inductors (MLCs), many of which contain soft ferrites, and which often require hexaferrites for high frequency applications. Such materials are made of layers of low-temperature co-fired ceramics (LTCCs), where the various ceramics layers (thick or thin films) such as magnetic and dielectric ceramics are co-fired with layers of metal paste or printed metal electrodes in a single chip. For reasons of its high conductivity, lower cost, and lower electrical losses, silver is usually the most suitable internal electrode material, but as it melts at 961 °C, all of the components must co-sinter sufficiently at temperatures below this, with ~900 °C typically being the goal. Gold and platinum (MP = 1064 and 1768 °C) are higher temperature electrodes but are also much more expensive, and copper (MP = 1084 °C) needs to be sintered in a reducing atmosphere to prevent oxidation problems. For this reason, there are many investigation into the use of sintering aids, additives that lower the sintering temperature of hexaferrites, ideally to below 960 °C.

Many sintering aids involve either the formation of relatively low temperature glassy phases (e.g. SiO₂, B₂O₃, Bi₂O₃) between the particles of the ceramic compound, or the addition/substitution of a low sintering oxide into the ceramic (e.g., CuO), to reduce the overall sintering temperature. For example, an undoped sample of BaM with a grain size of 1–2 μm had a density of 67% at 1100 °C, 72% at 1200 °C and was still only 82% dense at 1300 °C. However, with an addition of 0.55% silica this was drastically increased to 72% at 1100 °C, 91% at 1200 °C and 96% at 1300 °C [251], as the silica forms a glassy intergranular phase above 1050 °C [252]. The addition of silica with CaO has also been claimed to increase densification while reducing grain growth in M ferrites [253]. B₂O₃ has been found to help densification of BaM through liquid phase sintering below 1000 °C, but only leads to enhanced grain growth at levels exceeding 0.1 mol%. An addition of 0.1 mol% gave a 98% dense product at only 1000 °C, compared to 93% for undoped BaM with a grain size of 0.5 μm [254].

The densification of SrM is also enhanced by the addition of silica [255], and there are several proposed mechanisms for this effect. It is known that SrO preferentially reacts with silica forming a low viscosity liquid phase which aids sintering, but some strontium can be lost to the sample [256]. This is unlikely to be a factor as the material is usually pure M phase at the temperatures required to melt silica. Above 1075 °C Fe²⁺ ions appear in silica-doped SrM, and the conductivity increases sharply at levels over 0.4 wt.% silica because of this. As the concentration of Fe²⁺ ions increases the number of oxygen vacancies increase, and this in turn increases the rate of sintering, lowering the maximum densification temperature [257].

Co₂Z with 8 wt.% PbO–B₂O₃ glass added started to sinter at 800 °C, and the maximum densification rate was achieved at 890 °C. After sintering at this temperature for 2 h, a dense (5 g cm⁻³) single-phase Z ferrite was produced, with excellent magnetic properties [258]. Pb²⁺ and Cu²⁺ substituted Ba₂₄Pb₀.6Co₂Z and Ba₃Co₁.₈Cu₀.₂Z ferrites were found to sinter at ~1100 °C, but with reduced permeability [259], whereas Wang et al. reported good quality Cu²⁺ substituted Co₂Z with a substitution up to Co₁₄Cu₀.₆, which had a high density of 4.9 g cm⁻³, high permeability and very good magnetic properties at 1150 °C [260]. It was also found that iron non-stoichiometry could lower the sintering temperature of Z ferrites, with a reduction of the Fe:Co ratio from 12 to only 9.8 reducing the sintering temperature of (Ba–Sr)₃Co₂Z ferrites [261]. In a very complex system involving a copper and bismuth substituted (Ba–Sr) Z ferrite with such an iron deficiency, with the formula (2 + 3x)(Co₀.₆Cu₀.₄) O₃Ba₀.₈₃ₓ(1–x)Sr₀.₁₆₇(1–x)BiₓO (9.8–1.5x) Fe₂O₃, where x = bismuth substitution of 0.5–1.5 and pre-calculated at 1140 °C, a very low sintering temperature for Z ferrite was achieved when further doped with small amounts of Bi₂O₃ or LiBO₂ as glassy sintering aids. The authors claim to make a fully dense Z ferrite at only 950 °C, with a density over the theoretical maximum for Co₃Z, attributed to the bismuth substitution, with grain size <2 μm, a low Mₘ (<37 A m² kg⁻¹, attributed to non-magnetic Bi₃⁺ replacing Fe³⁺) and a Tₑ that increases with x to 460 °C [261]. It was found that an addition of 0.5 wt.% LiBO₂ could further increase density and permeability, with samples sintered at 925 °C having a density of 5 g cm⁻³ and a permeability of 7 at 300 MHz, although it would be interesting to see if the highly complicated and confusingly presented results of this article can be repeated.

Ba₁₂Sr₁₅Co₂Z had 80 wt.% PbO–20 wt.% Cu₂O glass added to it (as 0, 2, 5 and 10 wt.%), and it was found that 2 wt% glass gave a 97% dense Z ferrite at 1150 °C. For the samples with 5 and 10 wt.% glass,
the ferrite sintered at only 1000 °C, but density then decreased above 1100 °C as oversintering and DGG took place, and with 10 wt.% glass the M ferrite was always present as a second phase. All glass-doped samples had the M phase present at 1150 °C [262]. Investigation of the Zn substituted Ba3Co2(0.8-x)Zn0.4Cu2xFe24O41 found that the limit of Cu substitution was x = 0.3, and that for x = 0.2 a reasonably dense Z ferrite with good magnetic properties was formed at 1125 °C/4 h [263].

Submicron Co2Z powders made by a citrate process, which normally sintered at 1150 °C, were found to produce a seemingly single phase sintered Z ferrite at only 890 °C, with a permeability of 5, when 2 wt.% Bi2O3 was added [264]. Wang et al. made 1–4 wt.% Bi-doped, Cu-substituted Ba3-CO2-xCu2Fe24O41 (x up to 0.6), synthesised by the citrate method and sintered to over 95% density at only 900 °C for all samples, with extraordinarily high density and resistivity values of up to 5.2 g cm−3 and 4.8 × 109 Ω cm, and grain sizes below 2 μm [265]. These samples even had good magnetic properties, equalising the best routinely processed ceramic samples.

Copper substituted Ba2Zn2(1-x-y)Co2xCu2yY was formed as a single phase Y ferrite at 950 °C when y = 0.4, with good magnetic properties [266]. In further studies by the same authors, as the amount of Cu2 was increased to 0.4, nearly fully dense Y samples could be obtained at 1050 °C for all values of Co2, and samples were over 95% dense at 1000 °C [267].

5.10. Grain growth in hexagonal ferrites

The grain growth in hexagonal ferrites is most likely a combination of grain boundary movement and Ostwald ripening, and the latter seems the most likely process for the extreme growth seen during DGG [268], which often results in extremely acicular platelets instead of regular hexagons. In microstructural studies of BaM films it was found that a higher Ba content led to higher nucleation rates and lower growth rates, giving a finer grained product with smaller diameter:thickness ratios [269].

In structural studies of BaM films it was found that a higher Ba content led to higher nucleation rates and DGG [268], which often results in extremely acicular platelets instead of regular hexagons. In microstructural studies of BaM films it was found that a higher Ba content led to higher nucleation rates and lower growth rates, giving a finer grained product with smaller diameter:thickness ratios [269].

When up to 1 mol% B2O3 was added to BaM it was found to diffuse into the lattice over 1000 °C to form BaFe12−xB2O19, the material being a mixture of BaM, α-Fe2O3 and BaFe2O4 at temperatures below this. However, over 750 °C BaFe2O4 forms an intermediate with B2O3 which nucleates rapidly and causes growth with long or high temperature sintering. This enhances crystallisation, promotes BaM formation and reduces porosity of the system, but also forms acicular platelets which become larger and more elongated with increasing boria addition. With additions from 0.1 to 0.3 mol% the grain size does not increase too much, being 2–10 μm at 1200 °C and still no larger than 10 μm at 1400 °C, but with higher levels plates up to 50 μm long are formed. The acicular platelets form over 1250 °C, but as the a parameter increases in one direction the c parameter decreases, reducing the length of the c-axis but maintaining the cell volume. As the basal plane is no longer a regular hexagon, a third lattice parameter, b, is required to describe the width of the cell in the non-elongated axis, perpendicular to a. Thus as this elongated growth occurs the ratio of c:a decreases, and this may resemble the undetermined processes involved in DGG. The largest c:a ratio is seen with an addition of 0.2 mol% B2O3 or less, and the mechanism of boria addition to BaM is suggested to be the following: with boria addition of only 0.1 mol% it is taken into the core of the lattice, promoting ferrite formation by homogeneous nucleation. With an increase of up to 0.3 mol% the extra boria behaves as a molten flux allowing the transport of reaction species, so most of the additive is promoting reactions between crystals, instead of their formation. With further addition the boria melt is thick enough to leave layers of B2O3 in between reaction centres on the faces of the platy grains, but they will float on this layer and can grow out sideways, forming the elongated grains [270]. Another investigation into the addition of smaller amounts of boria to BaM agreed with these findings, with both 0.1 mol% and 0.2 mol% producing 0.5 μm grains at 1000 °C, but the large growth up to 10 μm at 1200 °C only occurred with 0.2% addition [254].

5.11. Grain growth inhibitors

The doping of SrM with La3+ and Zn2+ to make Sr1−xLaxFe12−xZn4O19 was found to reduce the grain size while still producing a sintered material. When x = 0.3 the product was 97% sintered at 1200 °C, but with a grain size of only 0.8 μm, increasing to several μm over 1250 °C [271]. Nb2O5 acts as a very
good grain growth inhibitor in the sintering of BaTiO$_3$ when added in quantities over 0.5 wt.% [256], and it has been used to produce nanocrystalline spinel ferrites [272].

Addition of Silica to BaM has been claimed to both promote and hinder grain growth in various amounts. It seems that grain growth occurs with an addition of below 0.55 wt.% as this is below the solubility limit of silica in BaM. Above this loading grain growth is suppressed even at 1250°C, either because of the impurity drag of solid phases on grain boundaries slowing their movement, or because the silica reduces Ostwald ripening by suppressing surface diffusion [273].

An addition of 0.2% Al$_2$O$_3$ to SrM inhibits grain growth even at temperatures of 1250 °C, giving a material consisting of grains 2–5 μm in diameter, compared to the large grains present in the undoped material from DGG at this temperature. Unfortunately the alumina also massively hinders densification, giving a product full of pores of the same dimension as the grains which is only 66% dense [274]. It was found in the same investigation that B$_2$O$_3$ has the opposite effect, giving a duplex structure consisting of smaller grains and pores under 10 μm wide interspersed with huge plates measuring 25 μm and over. Although silica is normally considered to cause grain growth, it has been reported that silica can reduce grain size in SrM, either by forming as a solid at grain boundaries, or by the drag of the segregated silica between grains preventing them from joining [275]. In extruded alumina fibres, in which an unwanted rapid formation of large α-alumina grains often occurs, SiO$_2$, MgO, P$_2$O$_3$, B$_2$O$_3$ and ZrO$_2$ have all been used as grain growth inhibitors [276]. Pullar et al. doped their sol–gel derived Co$_2$Z with an addition of 0.67 mol% CaO, equivalent to 1:10 Ca:Ba. Not only did this begin to form the Z phase at a lower temperature of 1150 °C, but DGG was greatly suppressed, with the sample consisting of equiaxed, less-platy looking hexagonal grains only 1–3 μm in diameter and 1 μm thick [75]. By the time the single phase Co$_2$Z had formed at 1200 °C at a lower than normal, DGG had occurred, although the grains were still more equiaxed than usual, and the crystallite size from XRD was ~100 nm, under half the size of their conventional Co$_2$Z at 1250 °C. They suggested that the rate of grain growth in the hexagonal plane was impeded by the segregation of calcium at the grain boundaries, allowing growth along the c-axis to “catch up”, reducing DGG, until the calcium begins to dissolve into the lattice at 1200 °C.

6. Magnetic properties of hexagonal ferrites

6.1. Magnetism in hexagonal ferrites

All hexagonal ferrites contain at least one large metal 2+ ion (usually Ba$^{2+}$ or Sr$^{2+}$), which causes a slight perturbation in the lattice due to size differences, and is responsible for the magnetocrystalline anisotropy (MCA) in hexaferrites. The most common hexagonal ferrites have a preferred axis of magnetisation along the c-axis, so loose crystals in an applied field will align themselves with the c-axis parallel to the field, showing a different XRD pattern to randomly oriented samples. The magnetic properties are different if measured in the direction of alignment – $M_s$ saturates at a lower applied field and $H_c$ is larger if the fields is applied parallel to the c-axis, compared to if a fields is applied perpendicular to this “easy” axis. The ratio of $M_s/M_1$ for isotropic unaligned samples is around half that for well oriented samples [8], and $T_c$ is also higher in the direction of the c-axis in oriented samples [277]. The degree of this MCA is given by the crystalline anisotropy, $H_A$, in A m$^{-1}$, and the anisotropy constant $K_1$ is a measure of the difficulty to move the magnetisation out of that direction in the crystal lattice. MCA is connected to the energy needed to turn a magnetisation vector from the preferred low energy, or easy direction, to a difficult, higher energy orientation, represented by the anisotropy constants $K_1$ and $K_2$. For single hexagonal crystals the total anisotropy energy is given by the sum $\sum_{K} = K_0 + K_1 \sin^2 \phi + K_2 \sin^4 \phi + \ldots$, where $K_0$ = the energy to magnetise the easy axis, and $\phi$ = the angle between the direction of magnetisation and the c-axis [278]. The higher order terms are not usually necessary for uniaxial ferrites, $K_0$ has a low value as the easy axis is a low energy orientation, and often even the second order term is not required. A high crystalline anisotropy is a prerequisite for a high coercivity, for example the anisotropy constants (measured in 10$^2$ J m$^{-3}$) for BaM are $K_1 > 3000$ and $K_2 = 0$, making it a very magnetically hard material suitable for permanent magnets [8]. Therefore, $H_A$ is proportional to $K_1$ (which is positive), and it is the contribution of the spin from the iron atom in
the five-coordinate trigonal bipyramidal site which causes the large anisotropy in the uniaxial ferrites [279].

However, most Y ferrites and all the Co₂ ferrites are ferroxplana [7,280], with a preferred direction of magnetisation either in the hexagonal basal plane, or in a cone at an angle to the c-axis. As in the uniaxial ferrites the magnetisation is locked rigidly in this orientation, but in the ferroxplana ferrites it can rotate within the plane or cone of magnetisation. The first order anisotropy constant, $K₁$, is positive for the uniaxial ferrites, but negative for the ferroxplana ferrites, indicating that the magnetisation is out of the c-axis. However, the second and third order constants $K₂$ and $K₃$ become more important, and often must be considered with the ferroxplana ferrites. The $K₂$ constant is positive and relatively large (but $< -K₁$) in ferroxplana ferrites with the easy axis in the basal plane, and therefore reduces the total anisotropy effect when added to a negative $K₁$, and with planar ferrites the anisotropy field in the basal plane, $H_A$, is proportional to $-(K₁ + 2K₂)$. $K₂$ is mostly attributed to the presence of Co²⁺ in octahedral positions, as it is usually negligible in hexaferrites containing another divalent ion, except for the Y ferrites where the absence of the five coordinate Fe³⁺ site accounts for the ferroxplana anisotropy [184]. In ferroxplana ferrites with an easy cone of magnetisation the third order constant, $K₃$, also becomes relevant, and increases with increasing amounts of Co²⁺, but although it is positive, it is $\sim 10^{-3}$ of the magnitude of $K₁$. Therefore, the negative $K₁$ usually still dominates in ferroxplana ferrites, indicating an easy plane of magnetisation.

The anisotropy energy is required only to move magnetisation out of the plane or cone, and although shape anisotropy will oppose rotation within the plane this is a weak energy compared to the crystalline anisotropy, $H_A$, which is high in all the hexagonal ferrites. Therefore, the magnetisation is able to rotate freely within this plane, and as a result the ferroxplana ferrites are not good permanent magnets, but the combination of high permeability and low coercivity makes them excellent soft magnets for use in electrical devices, and they suffer low magnetic losses at high frequencies. The $K₁$ constant dominates at lower temperatures and $K₂$ becomes more important at higher temperatures, resulting in the observed changes in anisotropy with temperature of the ferroxplana ferrites [184].

The MCA in ferrites originates from dipole–dipole interactions, which can be calculated from the net magnetic moment of the lattice, and spin–orbit coupling in which the spin direction of an ion is coupled to the lattice via the orbital momentum of the ion. This is difficult to calculate for BaM as although the ground state Fe³⁺ ions have known orbital moments, there are also exited states mixed into the ground state created by perturbations such as the unusual fivefold symmetry of the trigonal bipyramidal site, and these must be major contributors to the anisotropy constants [281]. If the La³⁺ ion is substituted for barium to make LaM, one of the iron ions must become Fe²⁺ to compensate for the trivalent ion, and Fe²⁺ has a large orbital moment and therefore larger spin orbit coupling. Because of this, the anisotropy constant for LaM is greater than for BaM [282]. Co²⁺ ions also cause large increases of anisotropy in spinels due to increased spin–orbit coupling, and this explains why the anisotropy constants of the Co₂ ferrites are so large [283].

The most important secondary form of magnetic anisotropy for hexagonal ferrites is induced uniaxial anisotropy, achieved by applying a magnetic field to a randomly oriented polycrystalline material as it cools down through the Curie point. A material with a high $T_C$ is needed to allow ion or hole diffusion, and this process is often used to manufacture oriented ferrite products. It is possible to produce a magnetically oriented sample of the ferroxplana ferrites, as the MCA perpendicular to the c-axis is much greater than the shape anisotropy parallel to the c axis [18]. In the ferroxplana Co₂ ferrites the suggested mechanism is due to the anisotropic partition of cations and vacant cation sites, resulting in a textured product in which the basal planes of the particles are all aligned [284].

### 6.1.1. Magnetic moments and superexchange in the hexagonal ferrites

Each S block consists of two layers of four oxygen atoms with three cations between each layer, in octahedral and tetrahedral sites having opposing magnetic spins. There are four octahedral magnetic moments and two opposing tetrahedral moments, giving a net total of two moments. The R block has five octahedral moments, but due to the effects of the large barium atom two of them are really distorted tetrahedral sites and so they oppose the other three octahedral sites. The moment of the five-coordinate trigonal bipyramidal site is aligned with three of the octahedral moments as it is a distorted octahedral site, and so the total also results in a net of two moments. The T section has...
six octahedral and two tetrahedral moments, but again two of the octahedral moments are aligned with the tetrahedral, giving a net of zero magnetic moments. The tetrahedral sites are formed by the two barium atoms distorting two trigonal bipyramidal sites [8].

S block = 2↑ tetrahedral and 4↑ octahedral = 2↑
R block = 1↑ trigonal bipyramidal and 3↑ 2↓ octahedral = 2↑
T block = 2↓ tetrahedral and 4↑ 2↓ octahedral = 0

These net values are only true if all the cations are Fe$^{3+}$, which has a magnetic moment of 5 $\mu_B$. For example in BaM, which consists of S + R, and therefore has a net magnetic moment of 4↑ = 20 $\mu_B$ (Fig. 30) [8]. In ferrites other than M, and in doped M ferrites, some of the cations are other metals with different magnetic moments, which may occupy different sites depending upon composition and temperature, and may occupy a fraction of the total number of a certain site. The opposing spins of the T block, which is antiferromagnetic if all the ions are identical, lead to the lower magnetic saturation values for the Y ferrites compared to the other hexagonal ferrites. This explains the many variations seen in the magnetic properties of the hexagonal ferrites with temperature and composition, but it also means that to calculate the magnetic moment of a compound the exact positions of all the cations must first be known. However, the contribution towards the moment of each site in a compound can still be summed up as:

M = 1↑ trigonal bipyramidal + 7↑ 2↓ octahedral + 2↑ tetragonal
W = 1↑ trigonal bipyramidal + 11↑ 2↓ octahedral + 4↓ tetragonal
X = 2↑ trigonal bipyramidal + 10↑ 4↓ octahedral + 2↓ tetragonal
Y = 8↑ 2↓ octahedral + 4↑ tetrahedral
Z = 1↑ trigonal bipyramidal + 15↑ 4↓ octahedral + 6↓ tetragonal
U = 2↑ trigonal bipyramidal + 22↑ 6↓ octahedral + 8↓ tetragonal

These orientations are depicted in Figs. 7–12. It should be noted that these are the moments for the molecular units of the ferrites, and not their unit cells. As all the Y ferrites and all Co$_2$ ferrites are ferroplana, their spins are opposed in the orientation of the plane or cone, and not parallel to the c-axis, as shown for Y ferrite in Fig. 10 and the T block in Fig. 31.

![Fig. 30.](image) Cross section of the BaM structure with the c-axis vertical, and spin orientation of the iron atoms shown by arrows. Net magnetic moment = 4↑ = 20 $\mu_B$, for BaM The layers containing barium atoms are mirror planes [8].
In metals the spins are linked by exchange interactions between the magnetic moments of directly neighbouring atoms, and this short range interaction is negligible over longer distances. However, in ferrimagnetic ferrites the magnetic ions are separated from one another by oxygen atoms making them too far apart for direct exchange, and there are also shielding effects from the oxygen lattice. In 1948 the idea of superexchange was suggested, which involves the non-magnetic oxygen atoms in the interactions [285]. The spins of opposing neighbouring ions are linked by interactions which take place via the intermediate oxygen atom (Me₁–O–Me₂), and this process is called superexchange. The superexchange interactions of the R and T blocks are depicted in Fig. 31. The magnitude of the exchange can be estimated from the Me₁–O–Me₂ distance and the angle formed by this, with a shorter distance and a larger angle strengthening the interaction. An angle of 180° gives the largest interaction and an angle of 90° the smallest, and the effect decreases rapidly with distance, becoming negligible over an Me–O distance of 3 Å [286]. It is these interactions which determine the spins of the ions detailed above.

6.1.2. Summary of magnetic properties of hexagonal ferrites

A better sintered, and therefore denser, ferrite has more magnetic moments per unit volume and hence a higher $M_s$, but the heat treatment needed to maximise densification also usually results in grain growth giving a multi-domain particle with a lowered coercivity as some of the domains will oppose one another. Therefore, the optimisation of magnetic properties in hexagonal ferrites is dependant upon the particle size of the starting material and the sintering conditions employed [287]. A material with high $M_s$ and $H_c$ can be made by mixing nanosized powders of a high $M_s$ magnet such as $\alpha$-iron and a high coercivity magnet such as Nd₂Fe₁₄B together, to form a composite magnet [288], and this would also work with ferrites. Clearly reducing the grain size to, or below, the domain size will raise the coercivity, but a material with magnetically aligned domains will also have a higher coercivity, and oriented single crystal materials will approach the theoretical maximum values permitted. Random and oriented BaM domains are show in Fig. 32. The magnetisation process under an applied field depends upon the size and shape of the ferrite particles. If it consists of plates under 5 µm the material is magnetically conditioned by rotational processes, with grain over 10 µm wall movement dominates, with the critical grain size falling at temperatures below room temperature [289]. Table 5 compares the magnetic properties of BaM, SrM, and the Co₂ hexaferrites, to highlight the variation with structure. The X-ray density, molecular mass, number of Bohr magnetons, measured $M_s$ at room temperature, calculated maximum $M_s$ at zero Kelvin and $T_c$ for a number of barium M, W, Y and Z ferrites are shown in Table 5.
6.2. BaM ferrite

BaM has 20 \( \mu_B \) and this gives it a high saturation magnetisation of 72 A m\(^2\) kg\(^{-1}\) and a high Curie temperature of 450 °C. It also has a high anisotropy constant, \( K_1 = 3.3 \times 10^6 \) erg cm\(^{-3}\), which give BaM a large crystalline anisotropy of 1352 kA m\(^{-1}\) (17 kOe) along the c-axis [8]. This uniaxial character gives BaM a large theoretical maximum coercivity of 594 kA m\(^{-1}\), although the reported \( H_c \) values for BaM prepared from standard ceramic methods are low, at around 159–255 kA m\(^{-1}\), because of the large grain sizes in such materials, but \( M_s = 70 \) A m\(^2\) kg\(^{-1}\) which is close to the maximum value [4].

Typically, there is disagreement over the critical single domain size for BaM. It was initially reported as being 1.3 \( \mu_m \) [8], experimental estimates gave a larger 1.8 \( \mu_m \) [291], others have reported it to be a much smaller 460 nm [292], and if calculated from Kittle’s theory (assuming a spherical shape) it should be between 0.3 and 0.9 \( \mu_m \) [293] – it is usually assumed to be some where between 0.5 and 1 \( \mu_m \). However, all of these values are large, compared to 0.24 \( \mu_m \) for cobalt metal and 28 nm for iron, and unusually this domain size increases with temperature so that a multi-domain grain will have fewer Bloch walls as temperature increases. This also means that the coercivity will increase with temperature in a polycrystalline material, for example from 135 kA m\(^{-1}\) at –200 °C to 255 kA m\(^{-1}\) at 25 °C and peaking at 380 kA m\(^{-1}\) at 250 °C, after which point \( H_c \) then decreases [4]. This was for 3 \( \mu_m \) grains, but the coercivity can be up to 40 times smaller in grains as large as 1 mm. In a study of the effect of sintering temperature (and hence grain size) on coercivity, BaM was made by a

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**Table 5**

Comparison of magnetic characteristics of BaM, SrM and Co\(_2\) hexagonal ferrites at room temperature, where n/a indicates the value is not available, and no precise value is given for \( H_c \) as it varies too much with processing methods and grain size. Anisotropy constants marked \( * \) are in fact \( K_1 + K_2 \) values. These values are taken from a number of sources, and represent what are generally taken to be the correct values for these ferrites, often measured in single crystal form. More information on each hexaferrite, and the variation in their reported properties, is given in the following sections.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Formula</th>
<th>( M_s ) (A m(^2) kg(^{-1}))</th>
<th>( H_c )</th>
<th>Isotropic ( M_r/M_s )</th>
<th>( H_A ) (kA m(^{-1}))</th>
<th>( K_1 ) (10(^5) J m(^{-3}))</th>
<th>( T_c ) (°C)</th>
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<tr>
<td>BaM</td>
<td>BaFe(<em>{12})O(</em>{19})</td>
<td>72</td>
<td>High</td>
<td>0.50</td>
<td>1353</td>
<td>3.3</td>
<td>450</td>
</tr>
<tr>
<td>SrM</td>
<td>SrFe(<em>{12})O(</em>{19})</td>
<td>92–74</td>
<td>High</td>
<td>0.50</td>
<td>1592</td>
<td>3.5</td>
<td>460</td>
</tr>
<tr>
<td>Co(_2)Y</td>
<td>Ba(<em>{2})Co(</em>{2})Fe(<em>{2})O(</em>{22})</td>
<td>34</td>
<td>Low</td>
<td>0.38</td>
<td>2228</td>
<td>–2.6°</td>
<td>340</td>
</tr>
<tr>
<td>Co(_2)Z</td>
<td>Ba(<em>{2})Co(</em>{2})Fe(<em>{2})O(</em>{21})</td>
<td>50</td>
<td>V.low</td>
<td>n/a</td>
<td>1035</td>
<td>–1.8°</td>
<td>410</td>
</tr>
<tr>
<td>Co(_2)W</td>
<td>BaCo(<em>{2})Fe(</em>{1})O(_{17})</td>
<td>~50</td>
<td>Low</td>
<td>n/a</td>
<td>1687</td>
<td>–3.5 to –5°</td>
<td>490</td>
</tr>
<tr>
<td>Co(_2)X</td>
<td>Ba(<em>{2})Co(</em>{2})Fe(<em>{2})O(</em>{16})</td>
<td>57</td>
<td>V.low</td>
<td>n/a</td>
<td>756</td>
<td>n/a</td>
<td>467</td>
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<tr>
<td>Co(_2)U</td>
<td>Ba(<em>{4})Co(</em>{2})Fe(<em>{3})O(</em>{60})</td>
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<td>Low</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>434</td>
</tr>
</tbody>
</table>

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Fig. 32. (a) Single crystal BaM plate (1 \( \mu_m \) thick) seen under a polarising microscope, in the virgin state. The stripes are magnetic domains [8]. (b) The same plate after magnetising, with the domains aligned [8]. (c) Domain walls in BaM ferrite, viewed along the c-axis. Colloidal suspensions of magnetite particles have been used to make the domain walls visible for this image [290].

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standard ceramic route and sintered between 1100 and 1350 °C, with an accompanying grain growth from 0.5 μm to several μm, and was measured along with a large single crystal of BaM. $H_c$ decreased massively from 318 kA m$^{-1}$ to 102 Am$^{-1}$ in these samples, producing a soft ferrite (Fig. 33). In the sample sintered at 1350 °C the XRD pattern resemble that of a textured M ferrite with stronger peaks in the [001] direction, suggesting that DGG was occurring with preferential growth in the hexagonal plane, perpendicular to the c-axis. There was a direct relationship between the reciprocal grain size and $H_c$ (Fig. 33), suggesting that the pinning of magnetisation at grain boundaries determines $H_c$, but this disappears in largemulti-domain grains, greatly lowering $H_c$ [294].

Although coercivity will increase with a decrease in grain size, especially below the single domain size [295], there is also a minimum grain diameter for maximum coercivity. This is 0.1 μm for BaM, as at smaller diameters the coercivity decreases greatly as the ferrite tends towards the superparamagnetic state, which has a coercivity of zero at around 10 nm [296]. Coercivity is not purely determined by domain structure, but is also affected by shape and magnetic anisotropy effects, and for this reason oriented samples can have increased coercivities. The effects of processing upon magnetic characteristics has been studied in much greater detail for BaM than that of the other ferrites, and the findings are summarised below.

In the standard ceramic preparation of BaM, iron oxide and barium carbonate are calcined at 1000 °C, ground, pressed and sintered at 1200–1400 °C in air. For the magnetic properties, the oxygen content of the atmosphere is most critical during the cooling down process after sintering. This gives a permanent magnet material with a high resistance for low losses, good chemical and thermal stability, and a high coercivity.

BaM has been made by standard ceramic methods from magnetite, recovered from recycled pickling liquors, to give a high coercivity product of 530 kA m$^{-1}$ after 1100 °C/3 h [297], and a sample made from haematite by the same process had a similar coercivity but an extremely high $M_s$ of 75 A m$^2$ kg$^{-1}$ [113], which is actually higher than the usually accepted maximum value, and may be due to some undetected impurities. A high coercivity of 517 kA m$^{-1}$ was also obtained in 1 μm BaM, which was made from a precursor powder of BaM ground to under 10 nm and then resintered at 1000 °C. The grains were still covered with a paramagnetic surface layer of amorphous grains 5–10 nm in diameter, and while this raised the coercivity it also resulted in a low $M_s$ of 55 A m$^2$ kg$^{-1}$ [298].

Chemical coprecipitation usually gives a product at a lower temperature and with a smaller grain size than standard ceramic methods, and BaM made by this process tends to have a higher $M_s$ [51], up to 64 A m$^2$ kg$^{-1}$ for 0.1 μm grains [299]. In a stoichiometric mixture fired at 925 °C/5 h $H_c = 400$ kA m$^{-1}$, but this can be increased by using iron deficient mixes, and with an Fe:Ba ratio of 10.6 a maximum coercivity of 475 kA m$^{-1}$ was achieved [52]. When coprecipitated iron(II) salts were rapidly oxidised, extremely fine BaM was formed as 80 nm hexagonal plates with a reasonable $M_s$ of 59 A m$^2$ kg$^{-1}$, but the coercivity was only 374 kA m$^{-1}$ [300]. It has been claimed that a ratio of Fe:Ba of

Fig. 33. Change in $H_c$ with sintering temperature, and therefore grain size, for BaM, and the direct relationship between $H_c$ and reciprocal grain size [294].
between 11 and 11.5 gives the best magnetic properties, as eliminates the presence of the non-magnetic \(\alpha\)-Fe\(_2\)O\(_3\) and BaFe\(_2\)O\(_4\) intermediate phases that may remain at higher temperatures (in this case 950 °C), and that extended heating times from 1 to 5 h greatly improves the magnetic properties as well [301]. Sudakar et al. formed single phase BaM from a stoichiometric precursor via their thermal gel-crystallisation process at only 750 °C, which had a high \(H_c\) of 398 kA m\(^{-1}\) but a very low \(M_s\) <2 A m\(^2\) kg\(^{-1}\), with a sub-domain grain size of 50 nm [302]. This is an extraordinarily high \(H_c\) for such small particles (as the authors noted, but did not explain), and the \(M_s\) was said to be so low due to surface demagnetisation effects dominating. This had grown to several hundred nm by 950 °C, with excellent magnetic properties of \(M_s = 52.1\) A m\(^2\) kg\(^{-1}\) and \(H_c = 358\) kA m\(^{-1}\) for such a low temperature [25].

 Nanocrystalline BaM has also been made from an alkaline metal chloride salt-melt at low temperatures. The material was amorphous at 600 °C, with \(M_s = 5.3\) A m\(^2\) kg\(^{-1}\) and \(H_c = 270.6\) kA m\(^{-1}\), but by 650 °C some BaM had crystallised and \(M_s\) had risen to 26.8 A m\(^2\) kg\(^{-1}\), and it was pure BaM at 700 °C with small grains 100 nm wide and 40 nm thick, \(M_s = 61.5\) A m\(^2\) kg\(^{-1}\), \(H_c = 374\) kA m\(^{-1}\) [303]. BaM made at the higher temperature of 900–1050 °C in a flux of only NaCl had vastly superior magnetic characteristics, with coercivities up to 378 kA m\(^{-1}\), a high \(M_s\) of 71.6 A m\(^2\) kg\(^{-1}\) and a very high remanence for an isotropic material giving an \(M_r/M_s\) ratio of 0.77 [60]. BaM single crystals made from the ion exchange of \(\gamma^\prime\)-ferrite by a salt-melt process also had a high \(M_s\) of 72 A m\(^2\) kg\(^{-1}\) [66].

BaM made from a non-stoichiometric aqueous sol–gel route at 900 °C/1 h with a grain size of only 200 nm had a high \(H_c\) of 470 kA m\(^{-1}\) but a low \(M_s\) of only 55.7 A m\(^2\) kg\(^{-1}\) [68]. Similarly sized BaM particles produced from an organic sol precursor at the same temperature had a much higher \(M_s\) of 70 A m\(^2\) kg\(^{-1}\) and a large \(M_r/M_s\) ratio of 0.57, but a low coercivity of only 240 kA m\(^{-1}\) [79]. It was shown to be important to prefire sol–gel derived BaM powders containing organic compounds if a high coercivity material is desired. In unprefired samples BaM was single phase at 1050 °C with a coercivity of 286 kA m\(^{-1}\) and \(M_s\) of 70 A m\(^2\) kg\(^{-1}\), but prefired samples gave BaM at a temperature 300 °C lower and with a much reduced grain size, and their properties were optimised at 900 °C when \(H_c = 474\) kA m\(^{-1}\) and \(M_s = 70\) A m\(^2\) kg\(^{-1}\) [67]. BaM was made as random polycrystalline fibres from an aqueous sol–gel route using stoichiometric precursors fired to 1000 °C, and the halide-based sol gave \(M_s = 63.8\) A m\(^2\) kg\(^{-1}\) and \(H_c = 428\) kA m\(^{-1}\) [304], while the halide-free nitrate-based sol had lower values of \(M_s = 58.4\) A m\(^2\) kg\(^{-1}\) and a higher \(H_c = 401\) kA m\(^{-1}\) [77], with a submicron grain size. When such BaM fibres were steamed to remove the halides, the halide-based BaM had vales of \(M_s = 56.6\) A m\(^2\) kg\(^{-1}\) and \(H_c = 389\) kA m\(^{-1}\) when steamed at only 700 °C/3 h, and the grains seemed to form linear aligned ridges 200 nm wide along the fibre axis [156]. When cooled down to 50 K, \(M_s\) increased to 87.7 and 83.0 kA m\(^2\) kg\(^{-1}\) and \(H_c\) decreased to 349 and 361 kA m\(^{-1}\) for BaM and SrM random fibres, respectively [304]. Magnetic measurements of the as-synthesised hydrothermal BaM hexagonal plates made by Liu et al. showed that \(M_s\) increased steadily with synthesis temperature and time, with \(M_s\) levelling out after 250 °C/15 h at ~50 A m\(^2\) kg\(^{-1}\) [161]. After reaction at 200 °C/4 h \(M_s = 24.5\) A m\(^2\) kg\(^{-1}\), and it increased linearly with reaction time to ~40 A m\(^2\) kg\(^{-1}\) after 250 °C/4 h. \(H_c\) was unaffected by reaction temperature, and remain around 110 kA m\(^{-1}\) as the temperature increased from 200 to 250 °C/4 h, although when reaction time was studied at a constant temperature of 250 °C, \(H_c\) peaked after reaction for 4 h (115 kA m\(^{-1}\)), and then decreased slightly with prolonged reaction. When sintered at 900 °C/2 h, \(M_s\) increased to 68.7 A m\(^2\) kg\(^{-1}\), but \(H_c\) showed virtually no change and remained small at 116 kA m\(^{-1}\) [161]. By comparison, the hydrothermal BaM made by X Liu et al. had \(M_s = 48\) A m\(^2\) kg\(^{-1}\) and \(H_c = 135\) kA m\(^{-1}\) (the peak \(H_c\) with 1.5 \(\mu\)m grains) as-synthesised at 230 °C/48 h, with \(M_s\) and \(H_c\) increasing to 64 A m\(^2\) kg\(^{-1}\) and 183 kA m\(^{-1}\) when sintered at 1000 °C/4 h [160].

An extremely fine grained BaM was made from citrate synthesis, having a grain size of only 50 nm at 600 °C, but the magnetic properties were unexpectedly low for an apparently single phase material, with a coercivity of only 46 kA m\(^{-1}\) and \(M_s = 32.8\) A m\(^2\) kg\(^{-1}\). This was proved to be caused by the extremely small size of the particles, as with an increase to 60 nm at 650 °C the coercivity rose to 318 kA m\(^{-1}\), although \(M_s\) was still very low and did not increase much with further heating [85]. The grain size was still below 100 nm at 800 °C, and the magnetisation values suggested that the ferrite, although no longer superparamagnetic, was still suffering from size effects such as demagnetisation, inhomogeneity effects and a non-magnetic surface layer [305]. BaM particles made from the glass
crystallisation method using fine filaments of B_2O_3 glass produced hexagonal platelets less than 0.1 \textmu m at 800 °C which grew to over 1 \textmu m at 1000 °C. Ms and Hc reached maximum values of 75 A m\(^{-2}\) kg\(^{-1}\) and 456 kA m\(^{-1}\) at 900 °C [94]. Hollow spheres of pure BaM with diameters of only 90 nm were made from an aerosol spray, but they had poor magnetic properties of \(M_s = 38 \text{ A m}^{-2} \text{ kg}^{-1}\) and \(H_c = 49 \text{ kA m}^{-1}\) even after annealing for 48 h. This was because the walls of the spheres were only 30 nm thick, and a high proportion of the material existed as non-magnetic surface layers several nm thick on both the inside and outside surfaces [106]. As-synthesised 60 nm BaM made by combustion synthesis with 11% carbon had \(M_s = 58 \text{ A m}^{-2} \text{ kg}^{-1}\) and \(H_c = 71.6 \text{ kA m}^{-1}\), and when this was sintered as a compact at 1100 °C/3 h, \(M_s\) reduced to 50 A m\(^{-2}\) kg\(^{-1}\) and \(H_c\) increased greatly to 239 kA m\(^{-1}\), with an AC conductivity of 10\(^7\) S m\(^{-1}\) at 10 MHz [104]. The \(M_s\) and \(H_c\) values for many M ferrites are summarised and compared in Table 7.

### 6.2.1. Magnetically oriented BaM

If the BaM is heated in a magnetic field before sintering, anisotropic materials can be produced which are tailored to be either remanence biased (high \(M_r\), low \(H_c\)) or coercivity-biased (high \(H_c\), low \(M_r\)), the remanence biased product having a very square loop with a sudden, almost vertical drop [306]. Magnetically anisotropic, oriented BaM was first made in 1954, and the remanence was found to be nearly doubled by this and the energy product quadrupled, but the coercivity was decreased [307]. To become oriented a polycrystalline ferrite must consist of grains over 0.1 \textmu m, but ideally below the domain size [253]. The shape anisotropy is very low compared to the large crystalline anisotropy, and in oriented polycrystalline samples \(M_s\) parallel to the \(c\)-axis was 70 A m\(^{-2}\) kg\(^{-1}\), but only 40 A m\(^{-2}\) kg\(^{-1}\) perpendicular to it. The remanence also varies greatly with orientation, with the ratio \(M_r/M_s\) being close to 1 along the \(c\)-axis in oriented BaM, but reduced to 0.5 in randomly oriented samples [4]. The effect of fibre alignment on magnetisation is discussed in Section 9.

### 6.2.2. Substituted BaM

The magnetic saturation of M ferrites can be increased with substitution by some non-magnetic ions, such as Zn\(^{2+}\). This is because the zinc ions greatly prefer tetrahedral positions, and in M ferrites the tetrahedral sites oppose the spin of most of the octahedral sites, which produce the net moment. Therefore, substitution with Zn\(^{2+}\) reduces this negative contribution, increasing the net magnetic moment [308]. Zn substituted BaM has a very square shaped loop with a sudden drop in remanence, a high \(M_s\) of 65 A m\(^{-2}\) kg\(^{-1}\) and a coercivity of 199 kA m\(^{-1}\), making it a suitable candidate for some magnetic recording applications [309]. BaFe\(_{11.5}\)Co\(_{0.5}\)O\(_{19}\) was made by ion exchange, and although the material was only 75% pure with a non-magnetic impurity the saturation magnetisation was high, and \(H_c\) rose with annealing temperature as more five-coordinate sites were occupied, although the

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**Table 6**

Some typical characteristics of hexagonal ferrites: X-ray density, molecular mass, number of Bohr magnetons, measured \(M_s\) at zero Kelvin and \(T_c\) for a number of barium M, W, Y and Z ferrites, where n/a indicates the value is not available, all summarised from Smit and Wijn [8].

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>(\rho) (g cm(^{-3}))</th>
<th>Molecular mass (g)</th>
<th>(\mu_B) Bohr magnetons</th>
<th>(M_s) at RT (A m(^{-2}) kg(^{-1}))</th>
<th>(M_s) at 0 K (A m(^{-2}) kg(^{-1}))</th>
<th>(T_c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaM</td>
<td>5.28</td>
<td>1112</td>
<td>20</td>
<td>72</td>
<td>&gt;100</td>
<td>450</td>
</tr>
<tr>
<td>Mn(_2)W</td>
<td>5.31</td>
<td>1573</td>
<td>29.2</td>
<td>59</td>
<td>97</td>
<td>455</td>
</tr>
<tr>
<td>Fe(_2)W</td>
<td>5.31</td>
<td>1575</td>
<td>28</td>
<td>78</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>NiFe(_2)W</td>
<td>5.32</td>
<td>1578</td>
<td>26.4</td>
<td>52</td>
<td>79</td>
<td>520</td>
</tr>
<tr>
<td>ZnFe(_2)W</td>
<td>5.34</td>
<td>1584</td>
<td>31.6</td>
<td>73</td>
<td>108</td>
<td>430</td>
</tr>
<tr>
<td>Mg(_2)Y</td>
<td>5.14</td>
<td>1346</td>
<td>6.9</td>
<td>23</td>
<td>~30</td>
<td>280</td>
</tr>
<tr>
<td>Mn(_2)Y</td>
<td>5.38</td>
<td>1406</td>
<td>10.6</td>
<td>31</td>
<td>&gt;40</td>
<td>290</td>
</tr>
<tr>
<td>Co(_2)Y</td>
<td>5.40</td>
<td>1410</td>
<td>9.8</td>
<td>34</td>
<td>&gt;40</td>
<td>340</td>
</tr>
<tr>
<td>Ni(_2)Y</td>
<td>5.40</td>
<td>1414</td>
<td>6.3</td>
<td>24</td>
<td>~24</td>
<td>390</td>
</tr>
<tr>
<td>Zn(_2)Y</td>
<td>5.46</td>
<td>1428</td>
<td>18.4</td>
<td>42</td>
<td>72</td>
<td>130</td>
</tr>
<tr>
<td>Co(_2)Z</td>
<td>5.33</td>
<td>2518</td>
<td>29.8</td>
<td>50</td>
<td>68</td>
<td>410</td>
</tr>
<tr>
<td>Cu(_2)Z</td>
<td>5.37</td>
<td>2536</td>
<td>27.1</td>
<td>46</td>
<td>&gt;60</td>
<td>440</td>
</tr>
<tr>
<td>Zn(_2)Z</td>
<td>5.37</td>
<td>2539</td>
<td>38.4</td>
<td>58</td>
<td>&gt;84</td>
<td>360</td>
</tr>
</tbody>
</table>
Table 7

RT \( M_s \) and \( H_c \) values for many M ferrites.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Synthesis/composition</th>
<th>( M_s ) (A m(^2) kg(^{-1}))</th>
<th>( H_c ) (kA m(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{BaM}</td>
<td>Single crystal</td>
<td>72</td>
<td>594 (max)</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Solid state ceramics, 1200 °C</td>
<td>Up to 70</td>
<td>Up to 255</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td>From steel waste liquors, 1100 °C</td>
<td>Up to 75</td>
<td>Up to 530</td>
<td>[113,297]</td>
</tr>
<tr>
<td></td>
<td>Ground to 10 nm and resintered, 1000 °C</td>
<td>55</td>
<td>517</td>
<td>[289]</td>
</tr>
<tr>
<td></td>
<td>Coppted, 925°C</td>
<td>64</td>
<td>Up to 475</td>
<td>[299,52]</td>
</tr>
<tr>
<td></td>
<td>Coppted and rapidly oxidised, 80 nm</td>
<td>59</td>
<td>374</td>
<td>[300]</td>
</tr>
<tr>
<td></td>
<td>Gel crystallisation, 950 °C, 100 nm</td>
<td>52.1</td>
<td>358</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>Salt melt, 700 °C, 100 nm</td>
<td>61.5</td>
<td>374</td>
<td>[303]</td>
</tr>
<tr>
<td></td>
<td>NaCl flux, 700 °C</td>
<td>71.6</td>
<td>378</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>Aqueous sol–gel, 900 °C, 200 nm</td>
<td>55.7</td>
<td>470</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>Organic sol–gel, 900 °C</td>
<td>70</td>
<td>286</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>Sol–gel, prefired, 1050 °C</td>
<td>70</td>
<td>286</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>Sol–gel derived fibres, 1000 °C</td>
<td>58.4–63.8</td>
<td>401–428</td>
<td>[304]</td>
</tr>
<tr>
<td></td>
<td>Hydrothermal, 250 °C/4–15 h, as synth</td>
<td>40–50</td>
<td>115</td>
<td>[161]</td>
</tr>
<tr>
<td></td>
<td>Hydrothermal, post-calcined 900–1000 °C</td>
<td>64–68.7</td>
<td>116–183</td>
<td>[161,160]</td>
</tr>
<tr>
<td></td>
<td>Citrate synthesis, 650 °C, 60 nm</td>
<td>46</td>
<td>318</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>Glass crystallisation, 900 °C</td>
<td>75</td>
<td>456</td>
<td>[94]</td>
</tr>
<tr>
<td></td>
<td>Hollow spheres, 30 nm wall</td>
<td>38</td>
<td>49</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>Combustion synthesis, as synth</td>
<td>58</td>
<td>71.6</td>
<td>[104]</td>
</tr>
<tr>
<td></td>
<td>Combustion synth, 1100 °C</td>
<td>50</td>
<td>239</td>
<td>[104]</td>
</tr>
<tr>
<td></td>
<td>Oriented BaM</td>
<td>( M_s ) = 70 \parallel H, 40 \parallel H</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>\textbf{Subs BaM}</td>
<td>Zn-subs BaM</td>
<td>65</td>
<td>199</td>
<td>[308]</td>
</tr>
<tr>
<td>BaFe(<em>{11.5})Co(</em>{0.5})O(_{19}), 800–1000 °C</td>
<td>51–65</td>
<td>151–175</td>
<td>[64]</td>
<td></td>
</tr>
<tr>
<td>BaFe(<em>{10.5})Co(</em>{0.25})O(_{17.05}), 15 min – 48 h exchange</td>
<td>45–60</td>
<td>49–119</td>
<td>[211]</td>
<td></td>
</tr>
<tr>
<td>BaFe(<em>{10})Zn(</em>{0.5})Ti(<em>{0.5})O(</em>{19}), 975 °C</td>
<td>60</td>
<td>160</td>
<td>[310]</td>
<td></td>
</tr>
<tr>
<td>Ba(_{1-x})La(<em>x)Fe(</em>{11.6})Zn(<em>x)O(</em>{19}), ( x = 0–0.8), 1975 °C</td>
<td>62–65</td>
<td>422–223</td>
<td>[313]</td>
<td></td>
</tr>
<tr>
<td>BaFe(_{12})B(<em>x)O(</em>{19}), 1400 °C</td>
<td>79</td>
<td>0.40</td>
<td>[270]</td>
<td></td>
</tr>
<tr>
<td>\textbf{SrM}</td>
<td>Single crystal</td>
<td>92.6–74.3</td>
<td>533–597</td>
<td>[130,184,319,325]</td>
</tr>
<tr>
<td></td>
<td>Solid state ceramic, 1000 °C</td>
<td>~70</td>
<td>286</td>
<td>[321]</td>
</tr>
<tr>
<td></td>
<td>Coppted, 950 °C, 200 nm</td>
<td>87</td>
<td>501</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>Sol–gel, 1000–1200 °C</td>
<td>56–70</td>
<td>414–263</td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td>Hydrothermal, calcined 1100 °C</td>
<td>64.5</td>
<td>300</td>
<td>[208]</td>
</tr>
<tr>
<td></td>
<td>Hydrothermal platelets, as synth</td>
<td>56</td>
<td>84</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td>Hydrothermal platelets, 1000 °C</td>
<td>76</td>
<td>150</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td>Hydrothermal, calcined 1250 °C</td>
<td>67.3</td>
<td>102</td>
<td>[181]</td>
</tr>
<tr>
<td></td>
<td>Sol–gel derived fibres, 1000 °C</td>
<td>63.3–65.0</td>
<td>440–453</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td>Steamed sol–gel fibres, 800 °C</td>
<td>81.4</td>
<td>457</td>
<td>[156]</td>
</tr>
<tr>
<td></td>
<td>Coppted, 900 °C</td>
<td>71.8</td>
<td>541</td>
<td>[325]</td>
</tr>
<tr>
<td></td>
<td>Citrate synthesis, 800 °C, 116 nm</td>
<td>67.7</td>
<td>517</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>Glass crystallisation, 54 nm</td>
<td>57</td>
<td>573</td>
<td>[326]</td>
</tr>
<tr>
<td></td>
<td>Ball milled 800 h, 13 nm</td>
<td>-</td>
<td>0.4</td>
<td>[321]</td>
</tr>
<tr>
<td></td>
<td>Oriented SrM</td>
<td>( M_s ) = 70 \parallel H, 40 \parallel H</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>\textbf{Subs SrM}</td>
<td>Sr(<em>{1-x})La(<em>x)Fe(</em>{12-2x})Co(</em>{19}), calcined 1215 °C</td>
<td>73 ((x = 0.18))</td>
<td>401 ((x = 0.15))</td>
<td>[329]</td>
</tr>
<tr>
<td>\textbf{PbM}</td>
<td>Sol–gel, 900 °C</td>
<td>54</td>
<td>398</td>
<td>[330]</td>
</tr>
<tr>
<td>\textbf{CoTiM}</td>
<td>BaCo(<em>{0.5})Ti(</em>{0.5})Fe(<em>{11})O(</em>{19}), 1000 °C</td>
<td>58.4</td>
<td>176</td>
<td>[199]</td>
</tr>
<tr>
<td></td>
<td>BaCo(<em>{0.7})Ti(</em>{0.3})Fe(<em>{10.8})O(</em>{19}), 1000 °C</td>
<td>56.6</td>
<td>45</td>
<td>[199]</td>
</tr>
<tr>
<td></td>
<td>BaCo(<em>{0.8})Ti(</em>{0.2})Fe(<em>{10.4})O(</em>{19}), 1000 °C</td>
<td>54.0</td>
<td>33</td>
<td>[199]</td>
</tr>
<tr>
<td></td>
<td>Coppted BaCo(<em>{0.7})Ti(</em>{0.3})Fe(<em>{10})O(</em>{19}), 1000 °C</td>
<td>55</td>
<td>75</td>
<td>[325]</td>
</tr>
<tr>
<td></td>
<td>Coppted BaCo(<em>{0.8})Ti(</em>{0.2})Fe(<em>{10})O(</em>{19}), 1000 °C</td>
<td>56</td>
<td>25</td>
<td>[325]</td>
</tr>
<tr>
<td></td>
<td>Melt flux BaCoTi Fe(<em>{10})O(</em>{19}), 980 °C</td>
<td>58</td>
<td>64</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>Sol–gel BaCo(<em>{0.5})Ti(</em>{0.3})Fe(<em>{11})O(</em>{19})</td>
<td>49</td>
<td>135</td>
<td>[340]</td>
</tr>
<tr>
<td></td>
<td>Sol–gel BaCo(<em>{0.7})Ti(</em>{0.3})Fe(<em>{10.8})O(</em>{19})</td>
<td>48</td>
<td>88</td>
<td>[340]</td>
</tr>
<tr>
<td></td>
<td>Sol–gel BaCoTiFe(<em>{10})O(</em>{19})</td>
<td>45</td>
<td>16</td>
<td>[340]</td>
</tr>
<tr>
<td></td>
<td>Glass Cryst BaCo(<em>{0.5})Ti(</em>{0.5})Fe(<em>{10.7})O(</em>{19})</td>
<td>60</td>
<td>125</td>
<td>[470]</td>
</tr>
<tr>
<td></td>
<td>Glass Cryst BaCo(<em>{0.5})Ti(</em>{0.5})Fe(<em>{10.7})O(</em>{19})</td>
<td>54</td>
<td>50</td>
<td>[470]</td>
</tr>
<tr>
<td>\textbf{Other subs M}</td>
<td>Citrate synth BaCoZr Fe(<em>{19})O(</em>{19}), 1300 °C</td>
<td>48</td>
<td>12</td>
<td>[343]</td>
</tr>
</tbody>
</table>
Curie point was unaffected by the substitution. After heating to 800 °C \( M_s \) was 51 A m\(^{-2}\) kg\(^{-1}\) and the coercivity was 151 kA m\(^{-1}\), at 900 °C \( M_s \) was 62 A m\(^{-2}\) kg\(^{-1}\) and at 1000 °C \( M_s \) was 65 A m\(^{-2}\) kg\(^{-1}\) and \( H_c \) was 175 kA m\(^{-1}\), as grain size increased from 90 nm to 200 nm [64]. Zn–Ti substitutions for iron in BaFe\(_{11.6} \cdot x \cdot z \cdot Zn_{x} \cdot Ti_{y} \cdot O_{19}\) sintered at 975 °C showed that, in a manner similar to the BaCoTiM ferrites, \( M_s \) was maintained at 60 A m\(^{-2}\) kg\(^{-1}\) while \( H_c \) was reduced as low as 160 kA m\(^{-1}\) for \( x = 0.6 \), while decreasing the Fe:Ba ratio to 10 decreased \( M_s \) and increased \( H_c \), as the crystallite size was <100 nm, below the domain size [310].

Lanthanide substituted BaM has been made with up to the total substitution of iron to give Ba-La\(_{1.2} \cdot O_{19}\) [192]. Lanthanum has also been added with an equal amount of a divalent ion to give the compounds Ba\(_{1-\cdot x} \cdot La_{\cdot x} \cdot Fe_{12-\cdot x} \cdot M_{C.2} \cdot O_{19}\) (Me = Zn or Mg) [311] and LaMFe\(_{1.2} \cdot O_{19}\) [312], and this increases both \( M_s \) and \( H_c \) compared to the undoped ferrite. LaM has also been reported as having an extremely large low temperature anisotropy of \( H_A \approx 3183 \) kA m\(^{-1}\) (40 kOe) [282]. La–Zn substituted Ba\(_{\cdot x} \cdot La_{\cdot x} \cdot Fe_{11.6-\cdot z} \cdot Zn_{\cdot z} \cdot O_{19}\) was made by a sol–gel route for \( x = 0–0.8 \), crystallising at 750 °C. When annealed at 975 °C it showed little change in \( M_s \) from 62 A m\(^{-2}\) kg\(^{-1}\) for \( x = 0 \) and 0.8, but with a peak of 65 A m\(^{-2}\) kg\(^{-1}\) for \( x = 0.4 \), and a large decrease in \( H_c \) from 422 to 223 kA m\(^{-1}\) with increasing \( x \) [313]. A study of RE\(^{3+}\)/Na\(^{+}\) substituted BaM showed that for Ba\(_{0.0} \cdot R E_{0.05} \cdot N a_{0.05} \cdot M \), \( M_s \) was fairly constant between 61.4 and 65.0 A m\(^{-2}\) kg\(^{-1}\), \( H_A \) was slightly lower than for BaM at 1265–1392 kA m\(^{-1}\) (15.9–17.5 kOe), \( T_r \) was slightly lower between 440 and 448 °C, and the in-plane anisotropy was higher, reflecting both the lowering of \( H_A \) and the more platy grain structure of the RE substituted M ferrites (Fig. 24) [205].

When coprecipitated iron-deficient BaM was doped with Nd\(_{2} \cdot O_{3}\) and sintered at 1000 °C/2 h, more than 7 mol% greatly reduced \( H_c \), but had little effect on magnetisation [209]. Cobalt–substituted oxygen-deficient BaFe\(_{10.5} \cdot C o_{0.25} \cdot O_{1.05}\) without a counterion for Co\(^{2+}\) and made by ionic exchange, had surprisingly good values of \( M_s = 45 \) A m\(^{-2}\) kg\(^{-1}\) and \( H_c = 119 \) kA m\(^{-1}\) after only 15 min of exchange. After 24 h of exchange, \( M_s \) had not changed much, but \( H_c \) had decreased to 83 kA m\(^{-1}\), and after annealing at 1100 °C/48 h this was further reduced to 49 kA m\(^{-1}\), with an increased \( M_s \) of 60 A m\(^{-2}\) kg\(^{-1}\) [211].

Antimony doped BaM up to \( x = 1 \) made by a hydrothermal process had nanosized acicular grains and a small coercivity (\( H_c = 36 \) kA m\(^{-1}\) ), and maintained the uniaxial anisotropy of the M ferrite, but the \( M_s \) was lowered by the formation of Sb\(_{2} \cdot O_{3}\) as a minor product [314], and BaM doped with arsenic and antimony made by a sol gel route also had drastically reduced magnetic properties and a grain size up to 6 μm [315]. BaM single crystals were made doped with Ti\(^{3+}\), which exhibited permivinvar behaviour with a loop closed in the centre at an applied field of zero T but open between 0.5 and 0.8 T, caused by a relaxation of Fe\(^{2+}\)/Ti\(^{4+}\) pairs [316].

Polycrystalline BaM was made by normal ceramic techniques with the addition of up to 1 mol% B\(_{2} \cdot O_{3}\) and the boria was found to exist in a molten state over 1000 °C, diffusing into the M structure to form BaFe\(_{12-\cdot x} \cdot B_{x} \cdot O_{19}\), and at temperatures over 1300 °C it caused large distortions in the lattice in amounts over 0.3 mol%. With 0.2 mol% addition \( M_s \) was raised by 13% to 79 A m\(^{-2}\) kg\(^{-1}\), because the non-magnetic B\(^{3+}\) ion substitutes for Fe\(^{3+}\) in tetrahedral sites, increasing the net spin. The boria also had a huge effect on coercivity and remanence, both decreasing with 0.2 mol% to very low minimum values of \( H_c = 400 \) A m\(^{-1}\) (5 Oe) and \( M_p/M_s = 0.2 \) after 1400 °C, the thousand-fold decrease in coercivity.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Synthesis/composition</th>
<th>( M_s ) (A m(^{-2}) kg(^{-1}))</th>
<th>( H_c ) (kA m(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol gel BaNi(<em>{0.75} \cdot Ti</em>{0.25} \cdot Fe_{0.5} \cdot O_{19})</td>
<td>850 °C</td>
<td>49.8</td>
<td>15</td>
<td>[69]</td>
</tr>
<tr>
<td>BaCo(<em>{0.2} \cdot S n</em>{0.17} \cdot Ti_{0.23} \cdot Fe_{0.85} \cdot O_{19})</td>
<td>50 nm</td>
<td>55</td>
<td>42</td>
<td>[469]</td>
</tr>
<tr>
<td>Citrate combustion Ba(MnTi(<em>{0.5} \cdot Fe</em>{1} \cdot O_{19})</td>
<td>900 °C</td>
<td>62</td>
<td>227</td>
<td>[98]</td>
</tr>
<tr>
<td>Citrate combustion Ba(MnTi(<em>{3}) \cdot Fe(</em>{8}) \cdot O(_{19})</td>
<td>900 °C</td>
<td>36</td>
<td>74</td>
<td>[98]</td>
</tr>
<tr>
<td>SrMg(<em>{2} \cdot Zr</em>{2} \cdot Fe_{12-\cdot x} \cdot O_{19})</td>
<td>52–44 nm</td>
<td>( H_c = 193 ) ((x = 0)), 15 ((x = 0.5)), 6 ((x = 1))</td>
<td></td>
<td>[350]</td>
</tr>
<tr>
<td>BaCo(<em>{0.2} \cdot Zr</em>{0.2} \cdot Fe_{11.825} \cdot O_{19})</td>
<td></td>
<td>57.7</td>
<td>380</td>
<td>[351]</td>
</tr>
<tr>
<td>BaCo(<em>{0.2} \cdot Zr</em>{0.2} \cdot Fe_{10.625} \cdot O_{19})</td>
<td></td>
<td>57</td>
<td>298</td>
<td>[351]</td>
</tr>
<tr>
<td>BaCo(<em>{0.2} \cdot Zr</em>{0.2} \cdot Fe_{11.125} \cdot O_{19})</td>
<td></td>
<td>55</td>
<td>158</td>
<td>[351]</td>
</tr>
<tr>
<td>BaFe(<em>{0.9} \cdot Al</em>{0.1} \cdot O_{19})</td>
<td></td>
<td>30.2</td>
<td>692</td>
<td>[351]</td>
</tr>
<tr>
<td>BaFe(<em>{1.2} \cdot Al</em>{0.2} \cdot O_{19})</td>
<td>900 °C</td>
<td>66.2</td>
<td>77</td>
<td>[161]</td>
</tr>
</tbody>
</table>
transforming BaM into a soft ferrite [270]. At 1000 °C $H_c = 223$ kA m$^{-1}$, the extremely low coercivity being associated with an increase in grain size up to 10 μm after 1400 °C/10 h, although these grains were still relatively small compared to the Y, Z and W ferrites at equivalent temperatures. The addition of 0.2–0.6% sodium to standard ceramic preparations increased density and coercivity slightly when added before calcination, but lowered them both when added after calcination but before sintering [54].

A silica dopant has been used to raise the energy product of BaM, and the magnetic properties of SrM have also been improved by the addition of CaO and SiO$_2$, dopants also used in doped W ferrites [317], and have an addition of 0.2% Al$_2$O$_3$ limits the grain size in SrM at high temperatures to under 5 μm, thus increasing coercivity [274]. The addition of silica with CaO has been claimed to reduce grain size and aid sintering in M ferrites, and a similar effect can be seen if BaO or SrO is used instead of CaO, but in this case the c and a lattice parameters shrink equally, maintaining the anisotropy of the crystal [253].

6.3. SrM ferrite

The magnetic properties of SrM have slightly higher values than those of BaM, and SrM has 20.6 μT. The Curie point is around 470 °C [130] and the anisotropy constant is $3.5 \times 10^6$ erg cm$^{-3}$ giving a very high $H_A$ of 1591 kA m$^{-1}$ (20 kOe) in the c-axis [318,319]. The saturation magnetisation of single crystal SrM has been variously reported at values between 92.6 A m$^2$ kg$^{-1}$ [130] and 74.3 A m$^2$ kg$^{-1}$ [184] (for single crystals), and the maximum coercivity is around 533 kA m$^{-1}$ [319], but polycrystalline samples rarely approach these high values. As with BaM, the values first reported for the coercivity of polycrystalline SrM were very low due to the large grain size of the early samples, and $H_c$ was typically reported as 240 kA m$^{-1}$ [320]. SrM made with standard ceramic methods with a wide diameter range of 0.5–50 μm has a reported coercivity of 286 kA m$^{-1}$ [321], and 0.1 μm specimens have been reported with $H_c = 517$ kA m$^{-1}$ [322]. SrM made from the standard ceramic route but then treated in nitrogen and hydrogen atmospheres before being recalcined in air gave a material with a much higher coercivity of 400 kA m$^{-1}$, and no loss of $M_s$, in a material with a grain size under 0.5 μm [178]. SrM sintered at 1200 °C/4 h had $M_s = 101.3$ A m$^2$ kg$^{-1}$ at 5 K [176].

Recently a fine grained (0.2 μm) sample has been made from coprecipitated salts, which when fired to 900–950 °C gave $M_s$ and $H_c$ which were both 94% of the single crystal values, at $M_s = 87$ A m$^2$ kg$^{-1}$ and $H_c = 501$ kA m$^{-1}$ [53]. SrM has also been successfully made from a sol gel precursor, which consisted of mixed phases with Fe$_2$O$_3$ as a minor product in the 800 °C and 1000 °C samples, but single phase SrM at 1200 °C. At 800 °C the ferrite had a low $M_s$ of 18 A m$^2$ kg$^{-1}$ due to it being an impure phase, and a very high $H_c$ of 557 kA m$^{-1}$ because of the small grain size. At 1000 °C $M_s$ had increased to 56 A m$^2$ kg$^{-1}$ and $H_c$ decreased to 414 kA m$^{-1}$, and in the pure M phase at 1200 °C $M_s = 70$ A m$^2$ kg$^{-1}$ and $H_c = 263$ kA m$^{-1}$ [80]. SrM made by a hydrothermal synthesis (Fe: Sr = 8) had $M_s$ of 64.5 A m$^2$ kg$^{-1}$, $H_c = 300$ kA m$^{-1}$ and $M_s/M_l$ of 0.5 when fired to 1050–1100 °C [208]. The extremely thin SrM platelets made by Y Liu et al. (Fe: Sr = 8) had good as-synthesised values of $M_s = 56$ A m$^2$ kg$^{-1}$ and $H_c = 84$ kA m$^{-1}$, which remained identical after heating to 500 °C (Fig. 23f), but improved to $M_s = 76$ A m$^2$ kg$^{-1}$ and $H_c = 150$ kA m$^{-1}$ after heating to 1000 °C, with little grain growth [91]. Ataie et al. reported that increasing the OH$^-$/NO$_3^-$ ratio from 2 to 6 increased grain size with a corresponding fall in $H_c$ from 92 to 54 kA m$^{-1}$, which coincided with a peak $M_s$ of 57.6 A m$^2$ kg$^{-1}$ in the as-synthesised SrM (5.6 × 1 μm platelets). Increasing the reaction temperature increased $M_s$ and decreased $H_c$ as the grains grew, whilst after 2 h reaction time there was little change in properties with longer synthesis [181]. When the SrM made at 220 °C/1 h (OH$^-$/NO$_3^-$ ratio = 2) was sintered at 1250 °C/1 h, it was 91% dense, with a grain size of 7.8 mm, $H_c = 102$ kA m$^{-1}$, $M_s = 67.3$ A m$^2$ kg$^{-1}$, and $H_A = 1393$ kA m$^{-1}$ (17.5 kOe).

SrM polycrystalline fibres were made via an aqueous sol–gel route using stoichiometric precursors fired to 1000 °C, and the halide-based sol gave $M_s = 63.3$ kA m$^2$ kg$^{-1}$ and $H_c = 453$ kA m$^{-1}$ [304], while the halide-free nitrate-based sol had higher values of $M_s = 65$ kA m$^2$ kg$^{-1}$ and a slightly lower $H_c = 440$ kA m$^{-1}$ [77], perhaps because it developed SrM at a lower temperature. When such SrM fibres were steamed to remove the halides, the halide-based SrM had values of $M_s = 55.1$ kA m$^2$ kg$^{-1}$ and $H_c = 369$ kA m$^{-1}$ when steamed at only 700 °C/3 h, and this increased greatly to
$M_s = 81.4 \text{ kA m}^{-2} \text{ kg}^{-1}$ and $H_c = 457 \text{ kA m}^{-1}$ when steamed between 400 and 800 °C/3 h, with none of the aligned linear ridges observed in the steamed BaM, and a grain size <100 nm [156].

As with BaM, the low coercivities of standard ceramic specimens can be increased greatly by reducing the grain size of the ferrite. Size can be reduced by milling, but the harmful effect of milling on coercivity is well established, and in SrM samples 2–3 μm in diameter $H_c$ was reduced to only 159 kA m$^{-1}$ after milling for 24 h [323]. After 80 h of ball milling such structural disorder had been imposed on the SrM that it had partially decomposed to α-Fe$_2$O$_3$, and superparamagnetic relaxation effects had reduced $H_c$ and $M_s$ significantly [324]. SrM made from the coprecipitation of chloride salts had a small grain size of 70 nm at 900 °C, and this resulted in very high coercivity in isotropic samples, with $M_s = 71.8 \text{ A m}^{-2} \text{ kg}^{-1}$. If a non-stoichiometric SrM was made with a small iron deficiency it was found that the coercivity was raised even higher, peaking at $H_c = 541 \text{ kA m}^{-1}$ with a Fe:Ba ratio of 11.6, compared to a theoretical maximum $H_c$ of 597 kA m$^{-1}$ [325]. Nanocrystalline SrM made from citrate precursors at 800 °C had a high coercivity and saturation magnetisation of 517 kA m$^{-1}$ and 67.7 A m$^2$ kg$^{-1}$ respectively, in a material with a grain size of 116 nm [85]. A material was made with the extremely high coercivity of 573 kA m$^{-1}$ but a lower $M_s$ of 57 A m$^2$ kg$^{-1}$ from a glass crystallisation method, which involved rapid quenching from 1400 °C. After annealing at 700 °C and leaching of the glass phase extremely small grains measuring 54 nm in the hexagonal plane and 41 nm in the c-axis were obtained, but they were also highly non-stoichiometric with a Fe:Sr ratio of only 8.8 [326]. SrM powder sized 0.5–50 μm was ball milled for 800 h to produce near-superparamagnetic sized powders of around 13 nm, which produced ferrite with a coercivity of 398 kA m$^{-1}$ after being fired at 1000 °C/4 h (with associated grain growth), despite the strain induced by the extended milling. After milling in a vacuum the ferrite powder was even smaller, around 8 nm, and mixed with 3 nm magnetite crystals [321].

Oriented SrM was produced using a standard ceramic sample milled to 0.8 μm, giving an oriented product in which $M_s = 70.7 \text{ A m}^{-2} \text{ kg}^{-1}$ and $H_c = 441 \text{ kA m}^{-1}$ [253]. Over 75% oriented SrM was made by pressing the submicron ferrite powder with 2–6% stearic acid in toluene, so that the hydrophobic end of the stearate bonded with the solvent and the hydrophilic end with the ferrite. The finely dispersed ferrite was then aligned and pressed in an external field before sintering. To achieve this degree of orientation the coercivity of the product first had to be reduced by milling the precursor to confer lattice strain, reducing $H_c$ from 438 kA m$^{-1}$ to below 318 kA m$^{-1}$ in samples fired to 1180 °C [327].

6.3.1. Substituted SrM

SrM has been doped with up to 1% La$_2$O$_3$, and a level of 0.7% was reported to be the optimum for raising $M_s$ and $T_c$ and gave a square loop, but also raised the crystallisation temperature to 1200 °C [328]. The substitution of rare earth metals into the Sr site of SrM was investigated for La, Sm and Nd in RE:Ba ratios between 1:16 and 1:2. Up to a ratio of 1:8 the $M_s$ stayed constant at around 65–67 A m$^2$ kg$^{-1}$, but it then decreased with increasing RE substitution, particularly for Nd. For La substitution, $H_c$ increased slightly and then decreased with more than 1/8, Nd had a small positive effect, and Sm increased $H_c$ considerably (by 25%), the effect seeming to stabilise at a ratio of 1:4. After an initial drop with 1:16 addition, all of the RE ions seem to increase the anisotropy field [187]. In a subsequent paper Wang et al. found that they could make Sr$_{1-x}$La$_x$M by hydrothermal synthesis when subsequently sintered up to 1300 °C, although for ratios of La:Sm > 1:8, they could not form the pure phase M ferrite, and had La$_2$O$_3$ and α-Fe$_2$O$_3$ as unreacted impurities, again stressing the difficulty of making pure LaM [208]. They also noted no significant change in microstructure up to a ratio of 1:8, but for 1:4 and 1:2 they saw wide and thin hexagonal plates develop, up to 5 μm in diameter, although these were symmetrical-looking hexagons, and there was no evidence that DGG had occurred. This change in microstructure was reflected in the magnetic properties of the ferrite powders: for La:Sm ratios of up to 1:8, there was almost no change in $M_s$ (~64.5 A m$^2$ kg$^{-1}$) with formation temperature, as also seen in their pure SrM sample. However, for a ratio of 1:4 the $M_s$ was considerably lower at 1000 °C (56 A m$^2$ kg$^{-1}$), and it only approached the $M_s$ of the other samples at 100 °C, and stabilised at ~63 A m$^2$ kg$^{-1}$ after this temperature. The 1:2 ratio sample was even more evident, with a linear increase from 44.5 A m$^2$ kg$^{-1}$ at 1000 °C to 62 A m$^2$ kg$^{-1}$ at 1300 °C – reflecting the higher temperature needed to synthesise the samples with more La, and the fact that they never form the single phase M ferrite, retaining non-ferromagnetic phases. A similar trend was seen in $H_c$, where the pure
SrM reached a maximum $H_c$ of $\sim 300 \text{ kA m}^{-1}$ at 1100 °C, after which it decreased at grain growth occurred.

The La substituted samples showed similar maximum values and a peak $H_c$, but the temperature of that peak increased with increasing La content, and for the ratio of 1:2, a much lower maximum $H_c$ value was obtained at 1250 °C of only $\sim 200 \text{ kA m}^{-1}$. Measurements of the anisotropy fields showed that while there was little change in the MCA, shape anisotropy played an important role, as small amounts of La substitution formed a microstructure which was favourable to coercivity, but for ratios >1:4 a less favourable microstructure of wide platy crystals was formed (resembling more the hexagonal ferrites). Wang et al. reported that in all cases RE substitution in SrM had little effect on $M_s$ but increased $H_c$ in all cases by up to 18% (Sm), 14% (Pr), 11% (Nd) and 5% (La) [207]. The substitution of SrM with La$^{3+}$ and Zn$^{2+}$ was found to enhance the magnetic properties, giving the compound Sr$^{1+x}$La$_x$Fe$_{12-x}$Zn$_x$O$_{19}$. The lattice constant decreased with $x$ as the substituted ions were smaller than Sr$^{2+}$ and Fe$^{3+}$, and for $x = 0.3$, $K_1$ was lowered by 10%. However, after firing to 1200 °C the grains were still only 0.8 μm resulting in a large $H_c$ of 374 kA m$^{-1}$, and $M_s$ was increased by 4% [271]. Sr$_{1-x}$La$_x$Fe$_{12-x}$Co$_x$O$_{19}$, sintered at 1215 °C and with $x = 0.05$–0.25, showed a maximum $H_c$ of 401 kA m$^{-1}$ for $x = 0.15$, and maximum $M_s$ of 73 A m$^{-2}$ kg$^{-1}$ for $x = 0.18$, while $T_c$ decreased linearly to a minimum of 430 °C for $x = 0.25$ [329].

6.4. PbM ferrite

Although PbM was the first M ferrite to be characterised, its magnetic properties are inferior to those of SrM and BaM. The $K_1$ anisotropy constant is only $2.2 \times 10^6$ erg cm$^{-3}$ giving an anisotropy of 1090 kA m$^{-1}$ (13.7 kOe), which while considerably lower than the other M ferrites. PbM has a lower net moment of 18.6 μμ and $M_s$ is also low at 56 A m$^{-2}$ kg$^{-1}$, but the Curie point is similar to that of the other M ferrites at 452 °C [14]. Pure PbM has been made from the decomposition of a sol–gel precursor at 900 °C to give a material with high $M_s$ and $H_c$ values of 54 A m$^{-2}$ kg$^{-1}$ and 398 kA m$^{-1}$ [330]. When PbM was doped with Ga$^{3+}$ the compound PbGa$_x$Fe$_{12-x}$O$_{19}$ was made up to full substitution at $x = 12$. However, with increasing gallium substitution the magnetisation decreased until the compound became totally non-collinear at $x = 6$ with an $M_s$ of zero [331].

6.5. Co–Ti substituted M ferrites

The most important substituted M ferrites are the cobalt–titanium substituted ferrites, BaCoTiM (BaCo$_x$Ti$_{1-x}$Fe$_{12-2x}$O$_{19}$), of major commercial interest in the magnetic recording industry, and also for their variable anisotropy and microwave properties. Although other substituted ferrites are looked at in Section 5.6, the CoTiM ferrites deserve their own section under M ferrites, as they have become so important. They were first synthesised in the 1960s as a way of lowering grain size and coercivity considerably without much loss of $M_s$ [332], and were commercially developed by Toshiba in the 1980s to give particles 50 nm wide and 15 nm thick with a coercivity of 159 kA m$^{-1}$ [333]. Since then coercivity has been lowered considerably with further substitution to give a series of ferrites with the formula BaCo$_x$Ti$_{1-x}$Fe$_{12-2x}$O$_{19}$, which can be tuned with a variation in $x$ to give the desired properties, reducing $H_c$ to a minimum value at $x = 1.2$ [184].

The axial anisotropy also reduces with substitution, until it becomes in-plane at $x = 1.3$ [334]. This is because although the Ti$^{4+}$ ion only substitutes in octahedral sites, the Co$^{2+}$ ion substitutes in tetrahedral sites and the trigonal bipyramidal site, which is the major contributor to the uniaxial anisotropy [335]. The Co$^{2+}$ ions were shown to be in tetrahedral positions with a value of $x < 0.8$ [336], and after this substitution level they begin to occupy the five-coordinate sites as well, and a cone of magnetisation begins to develop as a result of this non-collinearly, and this also has an effect of reducing $H_c$ [337]. The angle of the cone was calculated to be 61° from the c-axis at room temperature for a substitution level of $x = 1$ [280], and in a detailed neutron diffraction study on single crystals by Kreisel et al., the angle and anisotropy where calculated for $x = 0, 0.4, 0.8$ and 1.1, and are shown in Table 8 [30]. This study also showed the magnetic properties of Co–Ti substituted M ferrites to be temperature sensitive, particularly with higher levels of substitution, and suggested that although Ti$^{4+}$ has no magnetic moment, the Ti$^{4+}$ cation on the Fe(5) site interrupts the magnetic interactions in such a
way that the RS and R'S' blocks become magnetically decoupled, resulting in helicoidal conical magnetic structures which become more pronounced at lower temperatures, contributing to the anisotropy.

The values for the magnetic properties vary with morphology, purity and processing method used, but some values are mentioned for here for comparison. In standard ceramic specimens all heated at 1000 °C/5 h, for $x = 0.5$, $M_r = 58.4$ A m$^{-2}$ kg$^{-1}$, $H_c = 176$ kA m$^{-1}$ and $M_r/M_s = 0.49$; for $x = 0.7$, $M_r = 56.6$ A m$^{-2}$ kg$^{-1}$, $H_c = 45$ kA m$^{-1}$ and $M_r/M_s = 0.38$; for $x = 0.8 M_r = 54.0$ A m$^{-2}$ kg$^{-1}$, $H_c = 33$ kA m$^{-1}$ and $M_r/M_s = 0.35$ [338]; and for $x = 1.1$, $M_r = 56$, and for $x = 1.5$, $M_r = 48$ A m$^{-2}$ kg$^{-1}$ [199].

A detailed study of non-stoichiometric BaCo$_{11.6}$Fe$_{12}$Ti$_{0.4}$O$_{19}$ made by the citrate route produce subdomain sized particles with good magnetic properties below 1000 °C. Grain size was found to decrease with $x$, and $H_c$ decreased linearly from 378 kA m$^{-1}$ for $x = 0.2$–80 kA m$^{-1}$ for $x = 0.8$, and a very soft ferrite was achieved for $x = 1$, while $M_r$ values remained reasonably stable around 60–55 A m$^{-2}$ kg$^{-1}$ [339]. BaCo$_{11.2}$Fe$_{12}$Ti$_{0.8}$O$_{19}$ made from precipitated chloride salts and fired to 900 °C had comparable values with standard samples, with $M_r = 55$ A m$^{-2}$ kg$^{-1}$ and $H_c = 75$ kA m$^{-1}$ at $x = 0.6$. $M_r$ was 56 A m$^{-2}$ kg$^{-1}$ and $H_c = 25$ kA m$^{-1}$ at $x = 0.85$. Even after firing the material at 900 °C for 24 h $M_r$ only reached a maximum of 58 A m$^{-2}$ kg$^{-1}$ [325]. BaCoTiM has been made by melt-flux precipitation at 980 °C with a high $M_r$ of 58 A m$^{-2}$ kg$^{-1}$ and a coercivity of 64 kA m$^{-1}$ [62]. When made from a mixture of FeOOH, Ba(OH)$_2$ and cobalt and titanium alkoxides, the M phase always existed with some minor haematite impurity. None the less a good quality magnetic product was produced, with $M_r = 49$ A m$^{-2}$ kg$^{-1}$ and $H_c = 135$ kA m$^{-1}$ at $x = 0.5$, $M_r = 48$ A m$^{-2}$ kg$^{-1}$ and $H_c = 88$ kA m$^{-1}$ at $x = 0.7$ and $M_r = 45$ A m$^{-2}$ kg$^{-1}$ and $H_c = 16$ kA m$^{-1}$ at $x = 1$ [340]. A nanosized BaCoTiM ferrite was made from the stearic acid gel method, with a grain size of only 30 nm but a coercivity of 88 kA m$^{-1}$ for a substitution level of $x = 0.8$ [341]. The glass crystallisation method resulted in more loss of $H_c$ than in coprecipitated samples, probably through increased lattice diffusion, so that at $x = 0.65$, $M_r = 60$ A m$^{-2}$ kg$^{-1}$ and $H_c = 125$ kA m$^{-1}$, at $x = 0.85$, $M_r = 54$ A m$^{-2}$ kg$^{-1}$ and $H_c = 50$ kA m$^{-1}$ [325], and at $x = 0.9$ $H_c = 41$ kA m$^{-1}$ [470].

6.6. Other substituted M ferrites

Battle et al. showed that the 4+ non-magnetic counter ion in CoMe$^{4+}$M ferrites has a large effect on how much of the Co$^{2+}$ occupies tetrahedral sites, and thus how quickly substitution effects anisotropy and $H_c$. Indeed, with Ti$^{4+}$ the cobalt greatly prefers tetrahedral sites, which contribute little to reducing anisotropy, where as other ions such as Sn$^{4+}$ induce the cobalt into octahedral sites, causing a greater change at lower doping levels [342]. Many doped ferrites analogous to the CoTiM ferrites have been investigated, and CoZrM has been reported as having the largest drop in coercivity whilst maintaining $M_r$ [60]. CoZrM made from the citrate process had a very small coercivity of 12 kA m$^{-1}$ for an $M_r$ of 48 A m$^{-2}$ kg$^{-1}$ when fired to 1300 °C [343]. The BaZn$_{12}$Ti$_{0.4}$Co$_{11.6}$O$_{19}$ series has been investigated for $x = 0.1$–0.8, and while $H_c$ and grain size decrease with $x$, $M_r$ peaked at $x = 0.3$ with a value of 59 A m$^{-2}$ kg$^{-1}$. The formation temperature also increased with $x$, and the grains were extremely acicular, having dimensions of 150 nm long and 10 nm thick for $x = 0.5$ at 800 °C [303]. These specimens were made from the salt-melt method, but ZnTiM has also been made from a sol gel route at 850 °C, and at $x = 0.75$, $M_r = 49.8$ A m$^{-2}$ kg$^{-1}$ and $H_c = 15$ kA m$^{-1}$ [69]. Ni–Zn–TiM had a constant $M_r$ of 52.5 A m$^{-2}$ kg$^{-1}$ with increasing substitution, but $H_c$ decreased from 115 kA m$^{-1}$ at $x = 0.5$ to 40 kA m$^{-1}$ at $x = 1$, and

<table>
<thead>
<tr>
<th>$x$</th>
<th>Anisotropy constants (10$^5$ erg g$^{-1}$)</th>
<th>Anisotropy field $H_c^s$ (kA m$^{-1}$)</th>
<th>Type and angle</th>
<th>$M_r$ (A m$^{-2}$ kg$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>$K_1 = 5.38, K_2 = 0.07, K_3 = 0$</td>
<td>$H_c^s = 1206$</td>
<td>Axial, 0°</td>
<td>72</td>
</tr>
<tr>
<td>0.4</td>
<td>$K_1 = 1.95, K_2 = 0.15, K_3 = 0.01$</td>
<td>$H_c^s = 443$</td>
<td>~Axial, ~0°</td>
<td>70</td>
</tr>
<tr>
<td>0.8</td>
<td>$K_1 = 0.65, K_2 = 0.32, K_3 = 0.51$</td>
<td>$H_c^s = 157$</td>
<td>Cone, 25°</td>
<td>65</td>
</tr>
<tr>
<td>1.1</td>
<td>$K_1 = 1.02, K_2 = 0.69, K_3 = 0.23$</td>
<td>$H_c^s = 54$</td>
<td>Cone, 40°</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 8 Anisotropy values calculated for BaFe$_{12-2x}$Co$_x$Ti$_x$O$_{19}$ single crystals from neutron diffraction and magnetic data [30].
the anisotropy changed from uniaxial to planar [344]. There is also little loss of \( M_s \) with increasing substitution in BaCoSnM, which had a coercivity of 42 kA m\(^{-1}\) in coprecipitated samples at \( x = 1.4 \), which were still uniaxial with \( M_s = 56.2 \text{ A m}^2 \text{ kg}^{-1} \) and a high \( M_r/M_s \) ratio of 0.39 [345]. BaCoSnM was found to have a finer grain size but inferior magnetic characteristics than BaM. However, this can be optimised in mixed BaCo-Ti-SnM ferrites, with superior magnetic properties than pure BaCoSnM but a finer product than BaCoTiM [338].

A detailed study of non-stoichiometric BaM, Ti, Fe\(_{11.6-2x}\)O\(_{19}\) (M = Zn or Sn, \( x = 0.1–1 \)), synthesised by the citrate route to produce sub-domain sized particles at 1000 °C, was made by Mendoza-Suárez et al. [339]. They found that BaSn, Ti, Fe\(_{11.6-2x}\)O\(_{19}\) contained large amounts of \( \alpha \)-Fe\(_2\)O\(_3\) and poor crystallisation up to 950 °C, and for \( x = 0.2 \) small amounts of \( \alpha \)-Fe\(_2\)O\(_3\) still remained at 975 °C. The amount of \( \alpha \)-Fe\(_2\)O\(_3\) present increased with \( x \), and with \( x > 0.2 \) \( \alpha \)-Fe\(_2\)O\(_3\) was always detected even at 1000 °C. \( H_c \) decreased from \( \sim 278 \text{ kA m}^{-1} \) with \( x = 0.1 \) to \( \sim 119 \text{ kA m}^{-1} \) at \( x = 0.4 \), after which there was little variation with increasing \( x \), and \( M_s \) exhibited a very large decrease from \( > 60 \) to \( < 10 \text{ A m}^2 \text{ kg}^{-1} \) with increasing \( x \), although it was still reasonably high at \( \sim 50 \text{ A m}^2 \text{ kg}^{-1} \) for \( x = 0.4 \). BaZn, Ti, Fe\(_{11.6-2x}\)O\(_{19}\) showed good crystallinity from low temperatures, although there was still a very small amount of \( \alpha \)-Fe\(_2\)O\(_3\) present up to 975 °C. \( H_c \) decreased a little bit with \( x \), from \( \sim 239 \text{ kA m}^{-1} \) for \( x = 0.1 \) to \( \sim 159 \text{ kA m}^{-1} \) for \( x = 1 \), and \( M_s \) also showed a small decrease from \( \sim 65 \text{ A m}^2 \text{ kg}^{-1} \) to \( \sim 55 \text{ A m}^2 \text{ kg}^{-1} \). In both cases grain size decreased with increasing \( x \), but were always below 100 nm. It would seem that Sn\(^{2+}\) substitution provokes an increase in the crystallisation temperature of BaM, and that it also had a greater effect at reducing \( H_c \) with lower substitution levels than Zn\(^{2+}\) or Co\(^{2+}\).

BaCoSnM, Ti, Fe\(_{12-2x}\)O\(_{19}\) with a grain size of 50 nm by 20 nm had a low coercivity of 42 kA m\(^{-1}\) and \( M_s \) of 55 A m\(^2\) kg\(^{-1}\). However, after heating in a reduction atmosphere the magnetic properties were greatly changed. After 280 °C/4 h the coercivity had increased greatly to 107 and \( M_s \) slightly to 62 A m\(^2\) kg\(^{-1}\), whereas after reduction at 380 °C/4 h the coercivity had dropped back down to previous levels at 48 kA m\(^{-1}\) but the \( M_s \) has now increased to a massive 114 A m\(^2\) kg\(^{-1}\). These changes were due to the formation by reduction of cobalt metal at the lower temperature and \( \alpha \)-iron at the higher temperature, and the paramagnetic effects of the \( \alpha \)-iron also interfered with the superexchange interactions of the ferrite, changing the magnetic anisotropy from uniaxial to a cone at an angle to the c-axis [469]. Titanium was found to inhibit the transformation through reduction. In Ba(MnTi)\(_x\)Fe\(_{12-2x}\)O\(_{19}\) made from a citrate combustion route and heated to 900 °C, as \( x \) increased from 0.5 to 2, \( M_h \), \( M_t \) and \( H_c \) all decreased from 62 to 36 A m\(^2\) kg\(^{-1}\), 30.4 to 15.7 A m\(^2\) kg\(^{-1}\) and 227 to 74 kA m\(^{-1}\), respectively [98].

In the compounds BaA, Me, Fe\(_{12-2x}\)O\(_{19}\) where A = Ru\(^{4+}\) or Ir\(^{4+}\) and me = Co\(^{2+}\) or Zn\(^{2+}\), it was found that the substitution level at which the anisotropy transforms from axial to planar could be reduced from the value of \( x = 1.3 \) required for BaCoTiM. The A\(^{4+}\) ions substitute in the octahedral and tetragonal bipyramidal sites and the Me\(^{2+}\) ions in the tetrahedral and tetragonal bipyramidal sites, rotating the magnetisation from the c-axis to the hexagonal plane. Ti\(^{4+}\) ions only ever occupy the tetrahedral sites, and this explains the quicker transformation to planar anisotropy in these materials [346]. The crystalline anisotropy reaches a minimum value at this transition point. For example, in BaZnRuM at \( x = 0.25 \), \( K_1 \) has a value of \( 1.4 \times 10^6 \text{ erg cm}^{-3} \) and \( H_A = 279 \text{ kA m}^{-1} \) (3.5 kOe), whereas at \( x = 0.35 \) the anisotropy constant \( K_t \) has now changed sign to \( -0.9 \times 10^6 \text{ erg cm}^{-3} \) indicating a planar anisotropy and \( H_A = 139 \text{ kA m}^{-1} \) (1.75 kOe). At the transition level of \( x = 0.30 \) the anisotropy is very weak and \( K_1 = 0.3 \times 10^6 \text{ erg cm}^{-3} \), but there is little change in \( M_s \) and \( T_c \) over this transition. The transition level is also \( x = 0.3 \) for BaZnRuM, at \( x = 0.5 \) for BaZnM and at \( x = 0.6 \) for BaCoM [347]. BaFe\(_{11.6-2x}\)Ir, Co, O\(_{19}\) was made by a sol–gel route for \( x = 0–0.8 \), showing a small decrease in \( M_s \) from 62 A m\(^2\) kg\(^{-1}\) for \( x = 0 \) to 60 A m\(^2\) kg\(^{-1}\) for \( x = 0.8 \), but a much larger decrease in \( H_c \) from 435 to 27 kA m\(^{-1}\) with increasing \( x \) [313]. This huge drop in \( H_c \) was attributed to a reduction of the magnetocrystalline anisotropy by Kriesel et al., who found that single crystals had assumed planar anisotropy at \( x = 0.65 \) after being uniaxial at \( x = 0.4 \). This fast change of the anisotropy with respect to other hexaferrites was correlated to the Ir\(^{4+}\) substitution on the 4e bipyramidal Fe\(^{3+}\) site, which plays a key role in the magnetocrystalline anisotropy of M ferrites. They also reported a decrease in \( M_s \) from 71 to 61 A m\(^2\) kg\(^{-1}\) as \( x \) went from 0 to 0.65, with a large drop from \( M_s = 68.5 \text{ A m}^2 \text{ kg}^{-1} \) for \( x = 0.4 \), when the ferrite was still more or less uniaxial [348].
Another system analogous to BaCoTiM is that of BaBaCoZrFe_{12−x}O_{19}, which for x = 0−1.2 was shown to retain uniaxial anisotropy up to x = 0.6 (H_{c} = 653 kA m^{-1}), after which the ferrite becomes a softer ferrite, and at x = 1.2 it has planar anisotropy with H_{A} = 398 kA m^{-1}. M_{s} is ~ constant at around 68 A m^{2} kg^{-1} for x < 0.4, and then decreases with x to 33 A m^{2} kg^{-1} for x = 1.2. A greater drop than in BaCoTiM ferrites, while H_{c} also decreases greatly from 143 kA m^{-1} for x = 0.2 to a minimum of 0.8 kA m^{-1} at x = 0.8 [349]. SrMg_{x}Zr_{x}Fe_{12−x}O_{19} nanopowders (52−44 nm) were found to have a large decrease in H_{c} with x, going from 193 kA m^{-1} at x = 0, to 15.5 and 6 kA m^{-1} for x = 0.5 and 1, respectively [350]. The x = 0.5 sample also showed an increase in M_{s} to 68 A m^{2} kg^{-1}. In a study of an iron-deficient BaCo_{1−x}Zr_{x}Fe_{11.5−2x}O_{18.25} system, it was found that H_{c} decreased to 380, 298 and 158 kA m^{-1} for x = 0.2, 0.4 and 0.6 respectively, while M_{s} remained approximately constant between 55 and 57.7 A m^{2} kg^{-1} [351]. Zn^{2+} and Nb^{5+} were used as a charge compensated substitution for Fe^{3+} to make Sr(Zn_{0.7}Nb_{0.3})_{x}Fe_{12−x}O_{19} for x = 0−1, with a non-stoichiometric Fe: Sr ratio of 11.6 using a sol–gel route. The M phase was retained at all these levels, and M_{s} increased from 67 to a maximum of 73.3 A m^{2} kg^{-1} for x = 0.8, while H_{c} progressively decreased with x from 517 to 183 kA m^{-1}, for samples heated to 900–950 °C/5 h. T_{c} increased slightly with x, and the temperature dependence of coercivity was slightly positive and decreased with x, so that for x = 1 there was almost no change in H_{c} until near T_{c}, attributed to a non-collinear magnetic structure and local spin canting [352]. BaFe_{10}Al_{2}O_{19} has been found to have M_{s} = 30.2 A m^{2} kg^{-1} and very high H_{c} = 692 kA m^{-1} [353]. In hydrothermally as-synthesised BaFe_{11.3}Al_{0.7}O_{19}, a reaction time of at least 4 h was needed at 250 °C to produce M ferrite, and as with the pure BaM from the same process, M_{s} increased with reaction time and temperature, but never reaching the same value as the pure BaM. Coercivity was uniformly low (<85 kA m^{-1}) in all conditions. H_{c} increased with temperature as more M phase was formed, but reaction up to 25 h at 250 °C caused little increase in H_{c}. The reaction products had M_{s} = 35.5 A m^{2} kg^{-1} and H_{c} = 80 kA m^{-1} after 250 °C/4 h. M_{s} = 48.5 A m^{2} kg^{-1} and H_{c} = 84 kA m^{-1} after 250 °C/4 h, and after sintering at 900 °C/2 h M_{s} = 66.2 A m^{2} kg^{-1} and H_{c} = 77 kA m^{-1} [161].

6.7. Y ferrites

The Y ferrites all have lower magnetisation than the M ferrites, the highest being for Zn_{2}Y (18.4 μ_{B}, M_{s} = 72 A m^{2} kg^{-1} at 0 K) [8], and getting lower in the sequence Zn > Mn > Co > Ni [354]. At room temperature, Zn_{2}Y has M_{s} = 42 A m^{2} kg^{-1}, but the Curie point of Zn_{2}Y is only 130 °C, and it has a low crystalline anisotropy of only 716 kA m^{-1} (9 kOe) [8]. Ni_{2}Y made by Sudakar et al. at only 950 °C was a very soft ferrite, with M_{s} = 25.5 A m^{2} kg^{-1}, H_{c} = 16 kA m^{-1} and a T_{c} of 387 °C [25], and it has a higher H_{A} of 1100 kA m^{-1} (14 kOe) [8]. The magnetic properties of various Y ferrites are shown in Table 6.

CoY has the highest MCA of any hexagonal ferrite, uniaxial or ferroxyplana, with a (K_{2} + 2 K_{3}) value of −2.6 × 10^{3} J m^{-3}, K_{3} = 80 J m^{-3} and the crystalline anisotropy reported originally as H_{A} = 2228 kA m^{-1} (28 kOe) in the preferred plane and only 119 kA m^{-1} in the c-axis, all at room temperature [8]. CoY has a moment of 9.8 μ_{B}, the room temperature saturation magnetisation is 34 A m^{2} kg^{-1} and the coercivity is small, with a relatively high Curie point of 340 °C [8]. Because of this large negative anisotropy, from T_{c} to RT and below CoY has an easy plane of magnetisation at 90° to the c-axis, with H_{A} peaking at around RT. The Y ferrites may have larger negative K values because there is no five-coordinate site in the Y ferrites, which comes positive as the easy plane becomes a cone of magnetisation, the angle to the c-axis decreasing from 90° at 215 K to <70° at 77 K, with a K_{2} value of 200 J m^{-3} at that temperature (Fig. 34) [8]. This cone is enough to induce a spontaneous magnetisation along the c-axis at low temperatures, making CoY a hard magnet with a high M_{s} at 77 K. More recently sintered ceramic CoY has been reported by Obol and Vittoria as having H_{A} = 2944 kA m^{-1}, a volume magnetisation of 183 kA m^{-1}, and H_{c} = 4.4 kA m^{-1}, which was increased further to H_{A} = 3342 kA m^{-1} and H_{c} = 5.3 kA m^{-1} in oriented samples [356]. Randomly oriented polycrystalline CoY fibres sintered at 1000 °C/3 h had M_{s} = 32.8 A m^{2} kg^{-1}, M_{c} = 9.2 A m^{2} kg^{-1} and H_{c} = 30 kA m^{-1} [357], and CoY made from an EDTA complex had M_{s} = 28.8−33.4 A m^{2} kg^{-1}, and H_{c} = 15−6.7 kA m^{-1} [212]. The RT magnetic properties of some Y ferrites are shown in Table 9.
180° domain walls were first demonstrated in Zn$_2$Y [358], and since then Co$_2$Y has also been shown to contain stacked layers of domains of equal width separated by 180° walls (Fig. 35), giving the domains a rectangular and not a hexagonal shape [359]. A single domain crystal has also been seen to become split by a 180° domain wall as the magnetisation drops below $M_s$ [19].

6.7.1. Substituted Y ferrites

Sr$_2$Zn$_2$Y showed a strange, non-collinear magnetic structuring due to the Sr$^{2+}$ ion distorting the lattice [230], and therefore the replacement of barium with strontium in Y ferrites steadily reduced the permeability, but a 50% substitution of lead increased it dramatically [21]. Kimura et al. reported in 2005 [360] that single crystals of Ba$_{2-x}$Sr$_x$Zn$_2$Y form a non-collinear helical spin structure for values of $x$ between 1.0–1.6, which is modulated by applied magnetic field, producing a Y ferrite with exciting

Table 9

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Synthesis</th>
<th>$M_s$ (A m$^2$ kg$^{-1}$)</th>
<th>$H_c$ (kA m$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_2$Y</td>
<td></td>
<td>42</td>
<td>-</td>
<td>[8]</td>
</tr>
<tr>
<td>1000 °C</td>
<td></td>
<td>32.9</td>
<td>&lt;4</td>
<td>[361,267]</td>
</tr>
<tr>
<td>Zn$<em>{1.2}$Cu$</em>{0.8}$Y</td>
<td>1050 °C</td>
<td>34.5</td>
<td>6.8</td>
<td>[362]</td>
</tr>
<tr>
<td>Mg$_2$Y</td>
<td></td>
<td>23</td>
<td>-</td>
<td>[8]</td>
</tr>
<tr>
<td>Co$_2$Y</td>
<td>Sol–gel derived fibres, 1000 °C</td>
<td>34</td>
<td>4.4</td>
<td>[8,356]</td>
</tr>
<tr>
<td>EDTA complex synthesis</td>
<td>32.8</td>
<td>30</td>
<td>15–6.7</td>
<td>[357]</td>
</tr>
<tr>
<td>Mn$_2$Y</td>
<td>1000 °C</td>
<td>31</td>
<td>-</td>
<td>[8]</td>
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<tr>
<td>Ni$_2$Y</td>
<td>950 °C</td>
<td>25.5</td>
<td>16</td>
<td>[25]</td>
</tr>
</tbody>
</table>

Fig. 34. Left: Changes in $M_s$, $H_A$ and $(K_1 + K_2)$ with temperature for Co$_2$Y [8]. Right: Change in angle of magnetisation with respect to the c-axis with temperature for Co$_2$Y [8].
ME properties near room temperature when a field of 1–1.5 T is applied ($x = 1.5$). This step wise change in $M_s$ with applied magnetic field in a pure phase hexaplana ferrite appears to be an indication of such a change in magnetic structure, and signals it out as of interest for future investigation. The recent interest in these ME Y ferrites is discussed in Section 7.

In substitutions of Co with Zn to give the compound Co$_{1-x}$Zn$_x$Y fired at 1000 °C/10 h, $T_c$ falls linearly from 340 °C ($x = 0$) to 100 °C ($x = 1$). The $M_s$ values increased with addition, but they were lower than expected with $M_s = 26.6$ (instead of 34) and 32.9 (instead of 42) A m$^2$ kg$^{-1}$ for $x = 0$ and 1 respectively [361]. Zinc weakens the super interactions and lowers $T_c$, but there is no change in the spin directions so the net magnetic moment increases with addition. $M_s$ showed a peak of 34.9 eA m$^2$ kg$^{-1}$ at $x = 0.75$, but this was attributed to thermal agitation of the $x = 1$ compound at room temperature as $M_s$ showed a steady increase at when measured at 77 K. The low $M_s$ and $T_c$ values also suggest that perhaps the material was not single phase Y. When made from the coprecipitation of superparamagnetic $\delta$-FeOOH and heated to 1200 °C, Zn$_2$Y was produced in which the grain size = 2 µm, $M_s = 32.7$ A m$^2$ kg$^{-1}$ and $M_s/M_s = 0.06$ [213]. Other studies of the Co$_{1-x}$Zn$_x$Y system showed similar trends in $M_s$ values, and $H_c$ values decreasing steadily with $x$ from ~12.7 kA m$^{-1}$ for Co$_2$Y to <4 kA m$^{-1}$ for Zn$_2$Y [267]. Zn$_{1.2}$Cu$_{0.8}$Y sintered at 1050 °C ($\rho = 5.12$ g cm$^{-3}$) was reported has having $M_s = 34.5$ A m$^2$ kg$^{-1}$, $M_s = 4.05$ A m$^2$ kg$^{-1}$ and $H_c = 6.8$ kA m$^{-1}$, and in Zn$_{1.2-2.9}$Co$_{2-x}$Cu$_{0.8}$Y these values increased slightly with a small addition of Co$^{2+}$ up to $x = 0.1$, as did the density [362].

ZnMnY was found to have a volume magnetisation of 183 kA m$^{-1}$, $H_A = 756$ kA m$^{-1}$ and $H_c = 1.43$ kA m$^{-1}$ [363]. Other substituted Y ferrites reported by the same authors, made by the flux melt method in BaCO$_3$/B$_2$O$_3$ glass at 1200 °C, include Co$_{0.25}$Zn$_{1.75}$Y ($H_A = 1151$ kA m$^{-1}$, volume magnetisation of 159 kA m$^{-1}$, and $H_c = 0.318$ kA m$^{-1}$) and Mn$_{0.25}$Co$_{0.75}$ZnY ($H_A = 1958$ kA m$^{-1}$, volume magnetisation of 159 kA m$^{-1}$, and $H_c = 318$ kA m$^{-1}$), very soft ferrites with extremely small $H_c$ values [356].

6.8. Z ferrites

All the Z ferrites have a uniaxial anisotropy with spontaneous magnetisation in the c-axis, except Co$_2$Z which has a preferred plane at room temperature perpendicular to the c-axis [7]. Co$_2$Z goes through three major changes in MCA with temperature: Cone → (220 K) Plane → (480 K) Uniaxial. Co$_2$Z has a net magnetic moment of 31.2 $\mu_B$, giving it an $M_s$ of 69 A m$^2$ kg$^{-1}$ at 0 K and 51 A

![Fig. 35. Diagram of 180° domain structures in Y (left) and Z (right) ferrites [19].](image-url)
m² kg⁻¹ at RT, with an extremely small coercivity and a high Curie point of 410 °C [8]. It is also strongly anisotropic, with \((K_1 + 2K_2) = -1.8 \times 10^7\) J m⁻³ and \(K_3 = -12\) J m⁻³ at RT, and this gives a high \(H_A\) of 1035 kA m⁻¹ (13 kOe) in the plane [8], but an extremely low anisotropy of only 10 kA m⁻¹ (120 Oe) parallel to in the c-axis [199]. Below 220 K, when \(H_A\) reaches a trough of <400 kA m⁻¹, the easy plane becomes a preferred cone of magnetisation, and as temperature decreases both \(H_A\) and \((K_1 + 2K_2)\) increase, although the anisotropy constants never become positive, as they do with Co₂Y at low temperatures. After peaking around RT, at 480 K \(H_A\) reaches a minimum of zero, and above this temperature \(K_1\) becomes slightly positive as Co₂Z becomes uniaxial, until it reaches the \(T_c\) (Fig. 36) [8]. These changes in anisotropy and variations in the anisotropy constants \(K_1\) and \(K_2\) are caused by a strong temperature dependence of the choice of site of the cobalt ions. In the planar state the spin alignments of the Co²⁺ ions are 1.08\(^\dagger\) and 0.92\(^\dagger\), and they are all in octahedral sites, the same as in Co₂Y [22]. Despite going through at least three changes in anisotropy between 0 K and the Curie point, \(M_s\) decreases steadily and evenly, without any jumps, to zero at \(T_c\), and Co₂Z remains a soft ferrite at all temperatures.

In polycrystalline Co₂Z at room temperature domains as large as 2 μm have been found in 50 μm grains, and the domains are aligned in the plane perpendicular the c-axis, similar to Co₂Y [19]. Unlike in the Y ferrite however, the domains are not of even thickness, the structure consisting of alternating thick and thin domains oriented opposite to each other, separated by 180° domain walls (Fig. 35) [19]. When Co₂Z was made from a molten salt synthesis, an incredibly low coercivity was achieved as the grains grew to form large hexagonal plates 10–25 μm in diameter, but without DGG seeming to have occurred. This incurred in change in \(H_c\) from 48 kA m⁻¹ at 1100 °C to only 88 A m⁻¹ (1.1 Oe) at 1200 °C, an extremely soft ferrite, with almost no change in \(M_s\) of 43.5 A m⁻¹ kg⁻¹ [364]. Randomly ori-
entitled polycrystalline Co$_2$Z fibres sintered at 1250 °C/3 h had $M_s = 44.8$ A m$^2$ kg$^{-1}$, $M_r = 9.2$ A m$^2$ kg$^{-1}$ and $H_C = 19$ kA m$^{-1}$, for a grain size of >10 μm in which DGG had occurred [357]. An addition of 0.67 wt% Ca to these fibres, to form the doped Ba$_3$Ca$_{0.3}$Co$_2$Z, resulted in a single phase ferrite at 1200 °C with grains ~2 μm diameter without DGG occurring, but largely unchanged magnetic properties of $M_s = 45.7$ A m$^2$ kg$^{-1}$, $M_r = 11.5$ A m$^2$ kg$^{-1}$ and $H_C = 25$ kA m$^{-1}$. Despite their small dimensions (50 × 300 nm), the Co$_2$Z powders made from a citrate route and heated to 1150 °C had excellent values of $M_s = 47.2$ A m$^2$ kg$^{-1}$, $M_r = 8.6$ A m$^2$ kg$^{-1}$ and $H_C = 8.6$ kA m$^{-1}$. When they were heated to 1250 °C, with an increase in grain size to 3 μm, the only significant change was a reduction in $H_C$ to 5.3 kA m$^{-1}$ [86].

Single crystals 3 mm × 500 μm with the domains oriented exhibited a definite anisotropy of the magnetisation, with a high $M_s$ of 57 A m$^2$ kg$^{-1}$ in the hexagonal plane, but a low $M_s$ of 36 A m$^2$ kg$^{-1}$ in the c-axis. There was almost no hysteresis loop in the plane, whereas in the c-axis coercivity was higher but with a very low remanence, caused by the much higher number of domain walls to be crossed in this direction [19]. Oriented polycrystalline samples have been produced from sintering prefired Co$_2$Z in a magnetic field at 1260 °C, which show a fan like texture as the hexagonal crystals align their basal planes. This became more pronounced as the crystals grew with more sintering, with the best orientation achieved after DGG occurred at 1320 °C giving grains up to 250 μm wide, and after being fired at 1300 °C/24 h the oriented samples were denser than random samples [365]. A fibre-like texture was also achieved by sintering the grains in a rotating magnetic field, and these produced a denser product (97%) than the fan textured samples made in a static field, although density was not improved by DGG [221]. Despite its supposedly uniaxial nature, the Ni$_2$Z reported by Sudakar et al., made at only 950 °C, was a fairly soft ferrite with $M_s = 37.4$ A m$^2$ kg$^{-1}$, $H_C = 54$ kA m$^{-1}$ and a $T_C$ of 418 °C [25]. At RT, the uniaxial Zn$_2$Z has a positive $K_2$ value of 0.7 × 10$^5$ J m$^{-3}$, $M_s = 58$ A m$^2$ kg$^{-1}$ and a lower $T_C$ of 360 °C, while for Cu$_2$Z $M_s = 46$ A m$^2$ kg$^{-1}$ and $T_C = 440$ °C. The RT magnetic properties of some Z ferrites are summarised in Table 10.

### Table 10

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Synthesis/grain size</th>
<th>$M_s$ (A m$^2$ kg$^{-1}$)</th>
<th>$H_C$ (kA m$^{-1}$)</th>
<th>Ref.</th>
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<td>Salt melt synthesis, 1100 °C, 10 μm</td>
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<td>Sol–gel derived fibres, 1250 °C, ~10 μm</td>
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<td>25</td>
<td>[364]</td>
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<td>–</td>
<td>[8]</td>
</tr>
<tr>
<td>Zn$_2$Z</td>
<td>–</td>
<td>58</td>
<td>–</td>
<td>[8]</td>
</tr>
<tr>
<td>Sr$_3$Co$_2$Z</td>
<td>Sol–gel, 1200 °C</td>
<td>48.5</td>
<td>5.6</td>
<td>[224]</td>
</tr>
</tbody>
</table>

### 6.8.1. Substituted Z ferrites

Sr$_3$Co$_2$Z ferrite (Sr$_3$Co$_2$Fe$_{24}$O$_{41}$, sintered at 1200 °C/3 h) was first reported by Pullar and Bhattacharya [224] as having a $M_s$ of 48.5 A m$^2$ kg$^{-1}$ at 5 T, although the sample was still not saturated, and it was a very soft ferrite with $H_C = 5.6$ kA m$^{-1}$, with a crystallite size of 91 nm calculated from XRD. These authors reported a curious and drastic change in shape of the magnetisation plot at an applied field of 1.5 T (Fig. 37), and although they made reference to the non-collinear structure seen in Sr$_2$Zn$_2$Y, they could not explain this two-step magnetic process observed in a single phase ferrite. However, it was this report that drew the attention of Kitagawa et al. [366] to this material as a potential ME ferrite, as it now appears that this step wise change in $M_s$ with applied magnetic field in a pure phase hexaplanar ferrite can be an indication of possible non-collinear magnetic structures, with potential as ME ferrites. This is explored in more detail in Section 7. It was observed that for Ba$_1.5$Sr$_{1.5}$Co$_2$Z the anisotropy lay in the basal plane RT, and with increasing temperature up to 250 °C this angle slowly decreased from 90° to ~70°, at which temperature the angle began to rapidly decrease to ~20°.
at 300 °C, and the ferrite became fully uniaxial at 400 °C [226]. However, in oriented polycrystalline Sr$_3$Co$_2$Z the easy axis of MCA was in a cone at an angle of 52.3° to the c-axis at RT [367], and remained so up to 200 °C, before rapidly decreasing further to ~25° at only 250 °C, and moving fully to the c-axis at the same temperature as the other Co$_2$Z ferrites [226]. – so it is uniaxial at room temperature, despite being a very soft ferrite. From neutron diffraction data, the ions filling the ten different possible Wyckoff positions for iron and cobalt ions were obtained by Takada et al. This demonstrated that, while in Sr$_{1.5}$Ba$_{1.5}$Co$_2$Z cobalt occupies six sites (Me1(2a), Me2(4f), Me4(12k), Me5(4e), Me8(12k) and Me10(2d)), in Sr$_3$Co$_2$Z cobalt only occupies the first four of these [226]. This means that Co$^{2+}$ is not present in the Me8(12k) or Me10(2d) positions – in other words, it is not present at all in the R block of Sr$_3$Co$_2$Z at all, unlike in other Co$_2$Z ferrites (Fig. 38). This also resulted in the magnetic moment of the cobalt ions being quenched between 200 and 250 °C in Sr$_3$Co$_2$Z, 50–100 °C lower than the other Co$_2$Z ferrites. Takada et al. also observed the two-step magnetisation loop first reported by Pullar and Bhattacharya, and noted that in oriented polycrystalline samples this effect was much more pronounced than was seen in the Sr$_{1.5}$Ba$_{1.5}$Co$_2$Z magnetisation loops.

Ba$_3$(Co$_{1-x}$Zn$_x$)$_2$Fe$_{24}$O$_{41}$ sintered at 1200 °C showed a small linear increase in $M_s$ from 48.1 to 53.7 A m$^2$ kg$^{-1}$ and linear decrease in Curie point from 410 °C to 386 °C as $x$ (Zn content) increased from 0 to 1, while remaining a very soft ferrite with small $H_c < 3.5$ kA m$^{-1}$ [368]. As zinc is substituted for cobalt in the planar Co$_2$Z, the anisotropy constants become less negative until $H_A$ ~ 0 at $x = 1.5$, and with more zinc the anisotropy becomes positive as the ferrite become uniaxial [8]. Zhang et al. also made Ba$_3$Co$_{1-0.5}$Cu$_{0.5}$Z($x = 0–0.8$) was made from a citrate route and sintered to over 95% density at 1100–1150 °C, the sintering temperature decreasing with increasing $x$, and the grain size was between 1 and 2 μm for all samples. There was a small increase in $M_s$ with $x$, from 47 to 50 A m$^2$ kg$^{-1}$, and an initial decrease in $H_c$ from 8.6 kA m$^{-1}$ for $x = 0$ to 3.5 kA m$^{-1}$ for $x = 0.4$, before it increased again with further Cu substitution [370]. Iron deficient (Ba/Sr)$_3$Co$_2$Z was doped with RE ions using Tb$_4$O$_7$ and Gd$_2$O$_3$ oxides in a standard ceramic route. The systems 3(Ba$_{0.5}$Sr$_{0.5}$)$_2$CoO$_{2}$O$_{10.05}$Gd$_2$O$_{3}$.10.8Fe$_2$O$_{3}$ and 3(Ba$_{0.5}$Sr$_{0.5}$)$_2$CoO$_{2}$O$_{10.05}$Tb$_4$O$_{7}$.10.8Fe$_2$O$_{3}$ produced a pure Z phase at 1200 °C, but with larger grains than the pure iron-deficient Co$_2$Z at that temperature, and in the case of the Tb doped Z DGG had begun [371]. The substituted Sr$_3$Zn$_2$Z shows a lattice distorted by the Sr$^{2+}$ ion, reducing drastically the magnetic properties of the compound compared to Ba$_3$Zn$_2$Z [230], and the Z structure collapses with substitution of the barium by lead [21]. Substitution with La$^{3+}$ to give Ba$_{3-x}$La$_x$Co$_2$Z can be made up to $x = 0.4$, with a peak $M_s$ of 58 A m$^2$ kg$^{-1}$ for $x = 0.1$ [229].

Fig. 37. The hysteresis loop of Sr$_3$Co$_2$Z fired at 1250 °C/3 h, showing an unusual two-step hysteresis loop which has recently aroused interest in this ferrite as a potential multiferroic material (see Section 7) [224].
6.9. W ferrites

The first W ferrite to be discovered, Fe₂W, has a large saturation magnetisation ($M_s = 78 \text{ A m}^2 \text{ kg}^{-1}$) and coercivity, and the Curie point is also high at 455 °C. The crystalline anisotropy constant, $K_1 = 3.0 \times 10^6 \text{ erg cm}^{-3}$, is of a similar magnitude to that of BaM, but with contributions from the higher constants $H_A = 1512 \text{ kA m}^{-1}$ (19 kOe), greater than that of the M ferrites [8]. The uniaxial W ferrites not only have large crystalline anisotropies, but also high saturation magnetisations, which are caused by not just superexchange mechanisms across one oxygen atom (Fe–O–Fe), but also super-superexchange processes across two oxygen atoms (Fe–O–O–Fe) [372]. It has also been reported that SrFe₂W has $M_s$ 10% higher than SrM, and an almost-equal anisotropy field [282], and SrFe₂W had $M_s = 100.2 \text{ A m}^2 \text{ kg}^{-1}$ at 5 K [176]. The magnetic properties of various W ferrites are shown in Table 6.

Relatively few values seem to have been reported for the saturation magnetisation of Co₂W, perhaps because of difficulties in preparing the pure material, although it has an established high Curie point of 490 °C and is known to be a soft ferrite [17]. The $H_A$ of Co₂W has been reported as being 1687 kA m⁻¹ (21.2 kOe) [373]. Hongying et al. report that Co₂W made from a standard ceramic route at 1250 °C/3 h has $M_s = 54.78 \text{ A m}^2 \text{ kg}^{-1}$, $M_r = 5.03 \text{ A m}^2 \text{ kg}^{-1}$ and a low coercivity of $H_c = 467.5 \text{ A m}^{-1}$ (<6 Oe) [374]. Co₂W has a magnetic anisotropy in a cone at an angle reported as 68.5° [375] to 70° [8] from the c-axis at room temperature, but the large $K_1$ constant variously reported as $-5.0 \times 10^6 \text{ erg cm}^{-3}$ [8] or $-3.5 \times 10^6 \text{ erg cm}^{-3}$ [17] would suggest the ferrite to have a planar anisotropy. This deviation from the planar orientation is caused by the contribution of the two large and positive second and third order anisotropy constants, $K_2 = 0.8.0 \times 10^6 \text{ erg cm}^{-3}$ and $K_3 = 0.9 \times 10^6 \text{ erg cm}^{-3}$, and this is a particularly large value for the $K_3$ constant [17]. The Co²⁺ ions are mostly divided between the S block octahedral and tetrahedral sites, with 1.4 Co²⁺ in the octahedral S block sites, and a few in the R block octahedral sites [17,376]. Randomly oriented polycrystalline Co₂W fibres sintered at 1250 °C/3 h had $M_s = 44.2 \text{ A m}^2 \text{ kg}^{-1}$, $M_r = 24.7 \text{ A m}^2 \text{ kg}^{-1}$ and $H_c = 39 \text{ kA m}^{-1}$, for a grain size of >10 μm in which DGG had occurred [357].
The most important W ferrites for applications in electronic circuits are the Zn$_2$W series, which have a high $M_s$ but a low $H_c$, despite being strongly uniaxial. Pure SrZn$_2$W has a saturation magnetisation of up to 77 A m$^2$ kg$^{-1}$ and a coercivity of around 40 kA m$^{-1}$, and $M_s/M_r = 0.01$ [377], while for BaZn$_2$W, $M_s = 79$ A m$^2$ kg$^{-1}$, $H_A = 995$ kA m$^{-1}$ (12.5 kOe) [378], $H_c$ 8 kA m$^{-1}$ and $M_s/M_r = 0.01$ [381]. PbZn$_2$W is a borderline hard magnetic material, with a high $M_s$ of 53.99 A m$^2$ kg$^{-1}$ but a high $H_c$ of 88 kA m$^{-1}$; the Curie point is at 326 °C and $H_A = 939$ kA m$^{-1}$ (11.8 kOe) [379]. BaNi$_2$W also has a uniaxial anisotropy, $M_s \sim 60$ A m$^2$ kg$^{-1}$ and $H_c > 48$ kA m$^{-1}$ [380], and the Ni$_2$W made by Sudakar et al. had $M_s = 58.2$ A m$^2$ kg$^{-1}$, a large $H_c$ of 143 kA m$^{-1}$ and a high $T_c$ of 544 °C [25]. BaMg$_2$W has also been reported as being uniaxial [375].

6.9.1. Substituted W ferrites

Both $M_s$ and $H_c$ of the Zn$_2$W ferrites can be varied by the substitution of Zn$^{2+}$, which prefers tetrahedral sites, with divalent metal ions which either adopt octahedral positions or inhibit grain growth, and the magnetic properties tailored with careful addition [377]. With doped BaZn$_{2-x}$Co$_x$W prepared from the glass crystallisation method, $M_s$, $H_c$ and $M_s/M_r$ are reported to decrease with increasing cobalt substitution, to reported minimum values of $M_s = 74$ A m$^2$ kg$^{-1}$, $H_c = 8$ kA m$^{-1}$ and $M_s/M_r = 0.1$ for small grained samples around 1 μm in diameter fired to 1150 °C [381]. However, in samples of BaZn$_{2-x}$Co$_x$W prepared by standard ceramic methods and fired to 1270 °C/8 h, $M_s$ was reported to reach a maximum of 77.1 A m$^2$ kg$^{-1}$ at $x = 1.0$. This sample was also reported to be an n-type superconductor at $x = 1.0$, due to hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions in the S block, suggesting that it was not totally stoichiometric [382].

Sodium doped SrZn$_2$W had a grain size of only 0.5–1.5 μm at 1225 °C, with a coercivity of 138 kA m$^{-1}$ and $M_s = 60.5$ A m$^2$ kg$^{-1}$. After 1300 °C for only 30 min the grains had grown to 1.8–4.0 μm and $H_c$ dropped to 36 kA m$^{-1}$ with an increase in $M_s$ to 67.8 A m$^2$ kg$^{-1}$, and after 2 h at this temperature the grains had undergone DGG to become 3–60 μm in diameter, with a corresponding drop in $H_c$ to 14 kA m$^{-1}$ but no further increase in $M_s$. [235]. Zn$^{2+}$ was substituted with (Fe$^{3+}$/Li$^+$) to produce the ferrite SrZn$_{2-x}$(FeLi)$_x$W, made from finely ground oxide precursors $< 0.1$ μm in diameter. When $x = 0.5$, W ferrite was produced after 1100 °C/15 h, and all of the properties were increased to $M_s = 91$ A m$^2$ kg$^{-1}$, $H_c = 100$ kA m$^{-1}$ and $M_s/M_r = 0.036$. With further heating at 1320 °C/5 h there was no change in $M_s$ and the other values had fallen to un-doped levels, and with a substitution of over $x = 0.5$ the Li$^+$ ion distorts the lattice, drastically lowering $M_s$ [377]. Sr$_{0.9}$Ca$_{0.1}$Zn$_2$W which was made from a fine grained precursor had a domain-sized particle diameter of only 1 μm, and subsequently a high coercivity of over 290 kA m$^{-1}$ and a saturation magnetisation of 65 A m$^2$ kg$^{-1}$ at 1100 °C. On heating to 1300 °C the grains had grown, and although $M_s$ had increased to 85 A m$^2$ kg$^{-1}$ the coercivity had dropped to only 8 kA m$^{-1}$ [383]. When La$^{3+}$ was substituted for Ba$^{2+}$ to make Ba$_{1-x}$La$_x$Co$_2$W ($x = 0–0.2$), it was found that increasing $x$ increased lattice distortions and hence the formation temperature of the W phase from 1220 °C to 1238 °C, when made by a standard ceramic route. There was also evidence that some Fe$^{3+}$ → Fe$^{2+}$ to balance the charge of the added La$^{3+}$, with no change in the valency of Co$^{2+}$. $M_s$ generally increased with $x$ from 59.27 A m$^2$ kg$^{-1}$ for $x = 0.05$ to a maximum of 70.11 A m$^2$ kg$^{-1}$ for $x = 0.15$, while $M_s$ and $H_c$ both decreased with $x$ from 4.36 A m$^2$ kg$^{-1}$ and 387.9 A m$^{-1}$ for $x = 0.05$ to 3.85 A m$^2$ kg$^{-1}$ and 369.5 A m$^{-1}$ for $x = 0.2$, in samples sintered at 1250 °C/3 h [374]. Ba$_{0.9}$La$_{0.05}$Na$_{0.05}$Zn$_2$W had $M_s = 76$ A m$^2$ kg$^{-1}$, $H_c = 8$ kA m$^{-1}$, $T_c = 345$ °C and $H_A = 947$ kA m$^{-1}$ (11.9 kOe) [205].

Powders of BaNi$_{2-x}$Co$_x$Fe$_{16}$O$_{27}$ prepared at 1250 °C, where the substitution ratio $x$ was varied from 0.0 to 1.4, showed a decrease in $H_c$ of nearly 50% with increasing Co content, attributed to a reduction of the crystal anisotropy field by changing the easy-axis of magnetisation from-axis towards the basal plane, and there was a small increase in $M_s$ from ~60 to ~70 A m$^2$ kg$^{-1}$ with increasing $x$ [384]. Coprecipitated Ba(Co$_{0.5}$Zn$_{0.5}$)$_3$Fe$_{16}$O$_{27}$, heated at 1200 °C/2 h had a very low $H_c$ of 1.8 kA m$^{-1}$, and $M_s \sim 50$ A m$^2$ kg$^{-1}$. It showed a small peak in permeability of 1.4 at around 3 GHz, a very broad FMR around 6–9 GHz, and a dielectric resonance at around 11 GHz, with $\varepsilon_r \sim 6$ [385]. ZnMnY was found to have a permeability between 3–4 at MW frequencies, and showed a strong FMR at 8.5 GHz [363]. When 0.3 wt.% cobalt stearate (8.5 wt.% Co, used as a reducing agent), 0.3 wt.% SiO$_2$ and 0.7 wt.% CaO was added to SrFe$_2$W ferrite and sintered at 1160 °C/1.5 h in N$_2$, a single phase W ferrite was formed with the analysed composition of Sr$_{0.977}$Ba$_{0.088}$Ca$_{0.008}$Fe$_{15.84}$Fe$_{3.055}$O$_{27}$ and a density of 5.00 g cm$^{-3}$. This produced a hard ferrite with a volume magnetisation of 382 kA m$^{-1}$.
volume remanence of, $H_r = 189 \text{ kA m}^{-1}$, $T_c = 493 ^\circ\text{C}$, high anisotropy with $K_0 = 3.1 \times 10^5 \text{ J m}^{-3}$ and $H_A = 1303 \text{ kA m}^{-1}$, and a temperature dependence of $H_A$ which resembled that of M ferrite [386].

The RT magnetic properties of some W ferrites bare summarised in Table 11.

### 6.10. X ferrites

The first X ferrite discovered was the uniaxial Fe$_2$X, and this was found to have a high anisotropy of $1233 \text{ kA m}^{-1}$ (15.5 kOe), a high $M_s$ of 74.5 A m$^2$ kg$^{-1}$ and a high Curie point at 522 $^\circ\text{C}$ in polycrystalline samples [8]. When this was substituted with 0.3% Gd$_2$O$_3$ to BaO, $M_s$ and $T_c$ dropped slightly to 72.4 A m$^2$ kg$^{-1}$ and 512 $^\circ\text{C}$ respectively, but $H_A$ increased to 1417 kA m$^{-1}$ (17.8 kOe). It was found that instead of substituting for barium as intended, the smaller Gd$^3+$ preferred the octahedral sites to the Ba$^{2+}$ positions in the oxygen lattice [238]. A detailed investigation of the magnetic properties of the X ferrite system was made by Gu between 1991 and 1994 [240,387–389], who measured Fe$_2$X, Co$_2$X, Ni$_2$X, Zn$_2$X, Cu$_2$X, Mn$_2$X and Mg$_2$X, as well as the (Fe$_{1-x}$Zn$_x$)$_2$X and (Zn$_{1-x}$Cu$_x$)$_2$X systems. He found that for (Zn$_{1-x}$Cu$_x$)$_2$X, $l_B$ and $M_s$ increased with $x$, although for $M_s$ this was linear at RT, but non-linear for $x<0.2$ at 1.5 K, as initially Cu$^{2+}$ ions entered both tetrahedral and octahedral sites, until for $x>0.2$ they entered octahedral sites only as the tetrahedral sites were saturated [388]. For (Fe$_{1-x}$Zn$_x$)$_2$X he found that at 1.5 K $M_s$ increased linearly with $x$, but at RT $M_s$ initially decreased to a minimum value for $x=0.5$ (FeZnX), and then increased again, but to a lower value than for $x=0$. This minimum was attributed to a non-linear decrease in $T_c$ with $x$ being concurrent with a linear increase in $\mu_B$ with $x$ [389].

The findings for the unsubstituted X ferrites are summarised in Table 12. Recent findings by Kamishi-ma et al. give largely similar $M_s$ values for Co$_2$X, Ni$_2$X, Mn$_2$X and Cu$_2$X, despite casting doubt on the purity of Gu’s samples, with magnetisation plots from which RT $M_s$ of ~60–70 A m$^2$ kg$^{-1}$ can be estimated, and extremely narrow, soft magnetic loops observed [239]. Unfortunately, these authors only show the plots, and do not give any actual values for $M_s$ of $H_r$ for direct comparison.

At RT, Co$_2$X has been reported as having a preferred cone of magnetisation at an angle of 74° to the c-axis, with a weaker anisotropy of 756 kA m$^{-1}$ (9.5 kOe), a high $M_s$ of 57.1 A m$^2$ kg$^{-1}$, and a very low $H_c$ of only 4 kA m$^{-1}$ in single crystal samples [19]. This easy plane/cone of magnetisation moves to a

### Table 11

RT $M_s$ and $H_r$ values of some W ferrites.

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<thead>
<tr>
<th>Ferrite</th>
<th>Synthesis/grain size</th>
<th>$M_s$ (A m$^2$ kg$^{-1}$)</th>
<th>$H_r$ (kA m$^{-1}$)</th>
<th>Ref.</th>
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<td>[8]</td>
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<tr>
<td>Ni$_2$W</td>
<td>–</td>
<td>60</td>
<td>48</td>
<td>[380]</td>
</tr>
<tr>
<td>NiFeW</td>
<td>–</td>
<td>58.2</td>
<td>143</td>
<td>[25]</td>
</tr>
<tr>
<td>ZnFeW</td>
<td>–</td>
<td>52</td>
<td>–</td>
<td>[8]</td>
</tr>
<tr>
<td>SrZn$_2$W</td>
<td>Na-doped, 1225 $^\circ\text{C}$, 0.5–1.5 $\mu$m</td>
<td>60.5</td>
<td>138</td>
<td>[235]</td>
</tr>
<tr>
<td></td>
<td>Na-doped, 1300 $^\circ\text{C}$, 1.8–4 $\mu$m</td>
<td>67.8</td>
<td>36</td>
<td>[235]</td>
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<tr>
<td></td>
<td>Na-doped, 1300 $^\circ\text{C}$, 3–60 $\mu$m</td>
<td>68</td>
<td>14</td>
<td>[235]</td>
</tr>
<tr>
<td>PbZn$_2$W</td>
<td>–</td>
<td>54</td>
<td>88</td>
<td>[379]</td>
</tr>
<tr>
<td>SrZn$<em>{1.5}$(FeLi)$</em>{0.5}$W</td>
<td>Solid state ceramics, 1100 $^\circ\text{C}$</td>
<td>91</td>
<td>100</td>
<td>[377]</td>
</tr>
<tr>
<td>Sr$<em>{0.9}$Ca$</em>{0.1}$Zn$_2$W</td>
<td>Fine precursor, 1100 $^\circ\text{C}$, 1 $\mu$m</td>
<td>65</td>
<td>290</td>
<td>[383]</td>
</tr>
<tr>
<td></td>
<td>Fine precursor, 1300 $^\circ\text{C}$</td>
<td>85</td>
<td>8</td>
<td>[383]</td>
</tr>
<tr>
<td>Ba$<em>{0.05}$La$</em>{0.05}$Co$_2$W</td>
<td>1250 $^\circ\text{C}$</td>
<td>59.3</td>
<td>0.388</td>
<td>[374]</td>
</tr>
<tr>
<td>Ba$<em>{0.05}$La$</em>{0.05}$Co$_2$W</td>
<td>1250 $^\circ\text{C}$</td>
<td>70.1</td>
<td>0.370</td>
<td>[374]</td>
</tr>
<tr>
<td>Ba$<em>{0.05}$La$</em>{0.05}$Na$_{0.05}$Zn$_2$W</td>
<td>–</td>
<td>76</td>
<td>8</td>
<td>[205]</td>
</tr>
<tr>
<td>Ba(Co$<em>{0.5}$Zn$</em>{0.5}$)$_2$W</td>
<td>Copption, 1200 $^\circ\text{C}$</td>
<td>50</td>
<td>1.8</td>
<td>[385]</td>
</tr>
</tbody>
</table>

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R.C. Pullar / Progress in Materials Science 57 (2012) 1191–1334
uniaxial position in the c axis above 143 °C [20]. It also exhibits a sixfold magnetic symmetry with 60°, 120° and 180° domain walls [19]. The Curie point has been measured as 467 °C for Co2X and 435 °C for Zn2X, the highest values for Co- and Zn-containing hexaferrites [20]. Polycrystalline Co2X fibres synthesised at 1200 °C were reported to have $M_s = 45$ A m$^{-2}$ kg$^{-1}$, $H_c = 68$ kA m$^{-1}$ and $M_t/M_h = 0.38$ [76]. Ni2X has been reported by Sudakar et al. with $T_c = 482$ °C, $M_s = 53.6$ A m$^{-2}$ kg$^{-1}$, and a high coercivity of 199 kA m$^{-1}$ [25]. Small single domain Co2X with a small grain size of ~50 nm had $H_c = 27.5$ kA m, and as the size increased to 250 nm, $H_c$ decreased linearly to ~1.6 kA m$^{-1}$, and $M_t$ increased with grain size from 41 to 64 A m$^2$ kg$^{-1}$ [82]. However, these NPs had a highly non-stoichiometric surface, which will effect the magnetic properties of such small particles, especially if it contained non-magnetic species. In general, the wide variation in reported $H_c$ values may be due to the presence of undetected secondary phases, in this often difficult-to-make ferrite.

Sr2Fe2X had $M_s = 100.2$ A m$^2$ kg$^{-1}$ at 5 K [176]. Sr2Zn2X was sintered at 1400 °C/6 h and found to have $M_s = 79.4$ A m$^2$ kg$^{-1}$ and very low $H_c$ of 8 kA m$^{-1}$, with $H_A = 987$ kA m$^{-1}$ (12.4 kOe) [243]. Mössbauer spectra were also measured, and the extremely low coercivity coincided with rapid grain growth as the single X phase formed at the high temperature of 1400 °C. See Table 12 for other magnetic properties. The RE and sodium substituted Ba1.9La0.05Na0.05Zn2X had $M_s = 79.7$ A m$^2$ kg$^{-1}$, $H_c = 8$ kA m$^{-1}$, $T_c = 400$ °C and $H_A = 1003$ kA m$^{-1}$ (12.6 kOe) [205].

6.11. U ferrites

Until recently there were no magnetic characteristics reported for Co2U, except that it had a planar anisotropy. In 2001 Pullar et al. characterised Co2U fibres which had $M_s = 51.5$ A m$^2$ kg$^{-1}$ and a low $H_c$ of 47 kA m$^{-1}$ with a low remnant magnetisation of $M_r/M_s = 0.26$ [76], and in 2004 Lisjak et al. reported Co2U with $M_s = 51.5$ A m$^2$ kg$^{-1}$ and $T_c = 434$ °C [245]. They also reported a variable $H_c$ between low values of 14 kA m$^{-1}$ to high values of 127 kA m$^{-1}$ in samples made from high-energy milling and subsequent reaction of the stoichiometric oxides, and $H_c$ increased with decreasing calcination temperature and with increasing milling time. Co2U made via a stearic acid sol–gel method with a small grain size of ~50 nm had $H_c = 21$ kA m, had a maximum $H_c$ of 30 kA m$^{-1}$ when the grain size reached 80 nm, and as the size increased to 180 nm, $H_c$ decreased linearly to ~22.5 kA m$^{-1}$. The reduction below 80 nm was attributed the onset of superparamagnetism below the critical domain size of 80 nm [83,390]. $M_s$ increased with grain size from 41 to 64 A m$^2$ kg$^{-1}$, but these NPs had a highly non-stoichiometric surface, which would effect the magnetic properties of such small particles.

All the other U ferrites are axially orientated, and Zn2U has a $K_1$ constant of $1.4 \times 10^9$ erg cm$^{-3}$ giving a moderately strong $H_c$ of 764 kA m$^{-1}$ (9.6 kOe) [8]. Due to the large molecular size it has 60.5 $\mu_B$ [8], a saturation magnetisation of 54.9 A m$^2$ kg$^{-1}$ [23] and the Curie point is around 400 °C [8]. Zn2U single crystals were reported to have $M_s = 53$ A m$^2$ kg$^{-1}$ and $H_A = 799$ kA m$^{-1}$ [391]. Lisjak et al. [245,392] reported $T_c = 404$ °C and $M_s = 55–59$ A m$^2$ kg$^{-1}$ in Zn2U, with $H_c$ varying between 14 and 86 kA m$^{-1}$ in polycrystalline samples made from high-energy milling and subsequent reaction, and 40 kA m$^{-1}$ in samples made from topotactic reactions between M and Y ferrites. They also reported that Ni2U has $T_c = 454$ °C, $M_s = 46$ A m$^2$ kg$^{-1}$, and $H_c = 30$ kA m$^{-1}$ [245], while Sudakar et al. found similar values for Ni2U of $T_c = 426$ °C, $M_s = 48.1$ A m$^2$ kg$^{-1}$, but a very different high coercivity of 145 kA m$^{-1}$ [25], which could be due to an undetected hard ferrite impurity, or a much smaller grain

### Table 12

<table>
<thead>
<tr>
<th>X ferrite</th>
<th>$T_c$ (°C)</th>
<th>RT $M_s$ (A m$^2$ kg$^{-1}$)</th>
<th>1.5 K $M_s$ (A m$^2$ kg$^{-1}$)</th>
<th>$\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe2X</td>
<td>513</td>
<td>75.2</td>
<td>101.3</td>
<td>48.2</td>
</tr>
<tr>
<td>Co2X</td>
<td>501</td>
<td>69.0</td>
<td>96.0</td>
<td>46.3</td>
</tr>
<tr>
<td>Ni2X</td>
<td>513</td>
<td>64.1</td>
<td>86.5</td>
<td>41.7</td>
</tr>
<tr>
<td>Zn2X</td>
<td>431</td>
<td>73.1</td>
<td>113.5</td>
<td>55.0</td>
</tr>
<tr>
<td>Cu2X</td>
<td>494</td>
<td>66.9</td>
<td>92.5</td>
<td>44.7</td>
</tr>
<tr>
<td>Mn2X</td>
<td>453</td>
<td>62.0</td>
<td>102.6</td>
<td>48.9</td>
</tr>
<tr>
<td>Mg2X</td>
<td>475</td>
<td>61.2</td>
<td>92.0</td>
<td>43.3</td>
</tr>
<tr>
<td>Sr2Zn2X</td>
<td>437</td>
<td>79.4</td>
<td>120</td>
<td>56</td>
</tr>
</tbody>
</table>
size (<1 μm) near the critical domain size. The magnetic properties of the pure Cu$_2$U and other impure U ferrites recently reported by Chandra Dimra et al. are shown in Table 13. The Co$_2$U, Mn$_2$U and Mg$_2$U ferrites had particularly low coercivities of $\leq$8 kA m$^{-1}$, and low $M_r/M_s$ ratios of $\leq$0.10 making them very soft ferrites, and these are the smallest coercivities reported for U ferrites [246]. The Mg$_2$U and Co$_2$U ferrites showed multiple Curie points, probably due to the existence of a Z ferrite minor phase. These impurities may also have reduced $M_s$ values.

The detailed magnetisation loops of Sr$_4$Co$_2$U have not yet been published, but it seems to have a $T_c$ of $\sim$450 °C, and is a very soft magnet. It was reported as showing two Neel temperatures, a ferrimagnetic ordering below 420 °C showing uniaxial characteristics, and that the MCA rotates from uniaxial towards the hexagonal plane below 80°C, in a manner similar to Mg$_2$Y and Sr$_3$Co$_2$Z at RT [34].

7. The microwave properties of hexagonal ferrites

7.1. A brief theory of microwave resonance and losses in ferrites

Dielectric losses occur in materials due to the damping of the vibrations of electrical dipoles, and as well as intrinsic losses due to crystal structure, extrinsic losses due to impurities, porosity, and grain boundaries in polycrystalline materials, dominate at higher frequencies, causing a great decrease of permittivity in most materials at MW frequencies. However, the effective magnetic permeability, $\mu_{\text{eff}}$, is virtually independent of frequency, but there is a critical frequency, $f_c$, above which $\mu_{\text{eff}}$ falls rapidly as a function of frequency$^{-1}$ due to eddy current losses. This generally has a lower value for materials with a higher permeability, but is also related to the resistivity and thickness of the material. The critical frequency is given by the equation

$$f_c = \frac{4R}{\pi \mu_0 d^2} \quad (7.1)$$

where $R$ is the specific electrical resistance of the piece of material, $\mu_0$ the initial permeability and $d$ the thickness of the material. Despite being resistive materials however, the ferrites still have a limiting frequency [393].

This is because in ferrites $f_c$ is also connected to magnetic spin effects, so there is a gyromagnetic critical frequency, $f_g$, also known as the spin relaxation frequency. This is determined by the gyromagnetic ratio, $\gamma$, which is the ratio of the magnetic moment to torque for an electron, and is therefore independent of the dimensions of the sample. The gyromagnetic ratio has a value of 0.22 MHz m A$^{-1}$, and $f_g$ is given by the equation

Table 13
RT magnetic properties of some U ferrites.

<table>
<thead>
<tr>
<th>U ferrite</th>
<th>$T_c$ (°C)</th>
<th>$M_s$ (A m$^2$ kg$^{-1}$)</th>
<th>$M_r$ (A m$^2$ kg$^{-1}$)</th>
<th>$H_c$ (kA m$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$U$^a$</td>
<td>457</td>
<td>67</td>
<td>13.6</td>
<td>37.4</td>
<td>[246]</td>
</tr>
<tr>
<td>Co$_2$U$^a$</td>
<td>407, 427, 464</td>
<td>58</td>
<td>6</td>
<td>8.0</td>
<td>[246]</td>
</tr>
<tr>
<td>Zn$_2$U</td>
<td>400</td>
<td>54.9</td>
<td>–</td>
<td>–</td>
<td>[8]</td>
</tr>
<tr>
<td>Ni$_2$U</td>
<td>404</td>
<td>55–59</td>
<td>–</td>
<td>14–86</td>
<td>[245,392]</td>
</tr>
<tr>
<td>Cu$_2$U</td>
<td>454</td>
<td>46</td>
<td>–</td>
<td>30</td>
<td>[245]</td>
</tr>
<tr>
<td>Mn$_2$U$^b$</td>
<td>426</td>
<td>48.1</td>
<td>–</td>
<td>145</td>
<td>[25]</td>
</tr>
<tr>
<td>Mg$_2$U</td>
<td>452</td>
<td>70</td>
<td>10</td>
<td>23.9</td>
<td>[246]</td>
</tr>
<tr>
<td>Sr$_4$Co$_2$U</td>
<td>415</td>
<td>67</td>
<td>5</td>
<td>7.8</td>
<td>[246]</td>
</tr>
<tr>
<td>Mg$_2$Y</td>
<td>407, 447</td>
<td>53</td>
<td>2.5</td>
<td>4.0</td>
<td>[246]</td>
</tr>
</tbody>
</table>

$^a$ With BaFe$_2$O$_4$ impurity.

$^b$ With Z ferrite and α-Fe$_2$O$_3$ impurity.
where \( M_s \) = the saturation magnetisation [394]. This equation is true for all ferro- and ferrimagnetic materials, but in good electrical conductors the effect is swamped by eddy current effects [395]. The eddy currents also increase exponentially with temperature, but they are negligible at room temperature in materials with a good resistance such as most hexagonal ferrites, except those containing significant amounts of Fe\(^{2+} \) [396].

### 7.1.1. Ferromagnetic resonance (FMR)

It has been shown that if \( f_g \) is plotted against \( M_s/\mu_i \) over a range of frequencies, a variation in \( f_g \) is seen, caused by Bloch wall movement and/or the rotation of magnetic domains. If both phenomena have an effect of FMR, typically the domain wall resonances occur at a slightly lower frequency than those due to spin rotation. Having single-domain-sized particles will remove the domain wall resonance effects, otherwise a diffuse FMR peak or multiple peaks can occur. These phenomena result in a point where \( \mu_i \) increases slightly before dropping, resulting in a resonance frequency around \( f_g \), and this is named ferromagnetic resonance, or FMR [395]. This resonance can be seen if a plot is made of the two components of the complex permeability, the real permeability \( \mu' \), and the imaginary permeability, \( \mu'' \). In a static field \( \mu'' \) is lower than \( \mu' \), and the two values remain more or less constant at low and medium frequencies, rising slowly to a peak. As the magnetic losses increase at higher frequencies \( \mu' \) suffers a sudden decrease, but \( \mu'' \) remains constant at this point until it also drops at a slightly higher frequency. Just before \( \mu'' \) drops it experiences a slight increase from the FMR around the critical frequency \( f_g \), giving it a maximum value. This maximum in \( \mu'' \) should occur at the same frequency at which \( \mu' \) has dropped to half it’s original value, and this is the FMR frequency, \( f_r \), and it should equal or be very close to \( f_g \).

Hexagonal plates, needles or fibres could be randomly dispersed to give a high magnetic permeability to a composite, or oriented to give a high magnetic permeability for incident radiation of a particular polarisation. The EM impedance, \( Z \), can be given as

\[
Z = \left( \frac{\mu}{\varepsilon} \right)^{1/2}
\]

where \( \mu \) is the magnetic permeability and \( \varepsilon \) the dielectric constant. The reflectivity, \( R \), of a thick piece of material for a wave of normal incidence to the material is

\[
R = \frac{(1-Z)}{(1+Z)}
\]

Therefore, the larger the permeability the lower the reflectance, and alignment and aspect ratio effects can increase \( \mu \) [397].

The magnetic permeability and dielectric constant are frequency dependent, but while \( \mu \) falls rapidly above the critical frequency, \( \varepsilon \) decreases relatively much less at high frequencies. A dielectric companion fibre or filler can be used to give improved impedance matching.

The ability of the magnetisation to rotate within the easy plane in ferroxplana ferrites results in a high magnetisation even at high frequencies, where spinels are useless due to high energy losses. The ferroxplana ferrites have lower magnetic permeabilities than the uniaxial ferrites, but they still have high dispersion frequencies up to 100’s of MHz, and FMR in the GHz region. As their spins can rotate within the plane but cannot move out of it, the precession of the spins is more difficult, lowering the gyromagnetic constant and shifting the resonance frequency to higher values than for other ferrites with comparable permeabilities. In the ferroxplana ferrites with a plane rather than a cone of magnetisation this effect is strongest, so the Y ferrites and Co\(_2\)Z behave differently to the others at RT [7], and the FMR of Co\(_2\)Z has been investigated quite extensively.

The natural FMR frequency (\( f_r \)) is defined as the point at which \( \mu'' \) is a maximum and which coincides with the half peak value of \( \mu' \), where \( \mu' \) is the real permeability and \( \mu'' \) is the imaginary permeability. In materials with planar anisotropy the \( f_r \) will be governed by the rotational stiffness of the magnetisation within the ab plane as well as the stiffness out of the ab plane. The corresponding
anisotropy fields are $H_a$ and $H_o$ respectively, and these are connected to the anisotropy constants $K_1$, $K_2$ ($H_a$) and $K_3$ ($H_o$). The resonance condition is given by

$$2\pi f_r = \gamma \sqrt{(H_aH_o)} \tag{7.5}$$

and literature values for $H_a$ and $H_o$ will therefore give an indication of the FMR frequency expected for the Z, Y and W hexaferries studied here. Typically $H_a$ is much larger than $H_o$.

In a perfect single crystal, any shift in $f_r$ should be purely dependent on the orientation of the applied field relative to the crystal structure, giving a very narrow FMR peak. However, in polycrystalline sample with randomly oriented crystallites, the orientation varies through all possibilities, broadening the resonance absorption. Even an oriented polycrystalline sample will have demagnetising effects at pores, grain boundaries and inhomogeneous areas, broadening FMR, and an additional DC field will exist at such imperfections, inducing magnetic poles at the surfaces of such features, also contributing to FMR line broadening [1]. As FMR line width is related to magnetic losses, with a more lossy material having a broader FMR, in most real materials these extrinsic processes dominate and determine FMR line width. While a single crystal may have an FMR line width as low as $10^3 \text{ kA m}^{-1}$, for polycrystalline ferrites it will be $>10^3 \text{ kA m}^{-1}$ [1].

MW and FMR measurements of ferrites are usually made either on a solid ferrite block waveguide of certain dimensions, or on a composite of ferrite particles in a dielectric medium, often a paraffin wax, pressed into a toroidal shape. The effective permeability of the composite is measured, and as the properties of the wax are known, the permeability of the ferrite can be extracted from a suitable mixture equation. The Lichtenecker equation is usually applied to measurements if the loading of the ferrite in the wax composite is a low volume fraction, but it has been shown that for high volume fractions (>30%) either the Bruggeman effective medium theory, or “quasi-crystalline approximation with coherent potential” theory (QC-ACP, also known as GKM, after Gyorffy, Korringa and Mills) are much more accurate [398].

7.2. M ferrites

The FMR frequency ($f_r$) of BaM was first characterised as being around 50 GHz [8], and has since been reported as 43 GHz [399] and 46 GHz at zero field, increasing as a field is applied unless it is applied at angle of more than 70° to the c-axis in an oriented sample [400]. The smallest line width for a perfect BaM sphere is 1.2 kA m$^{-1}$, and in polycrystalline BaM is tens of kA m$^{-1}$ wide [401]. In light-weight mullite/quartz hollow microspheres (2–3 μm) coated with first a layer of TiO$_2$ and then BaM by sol–gel methods (total coating ∼100 nm), $f_r$ was reduced to 8.2–8.5 GHz [402]. Random BaM and SrM fibres were measured by Pullar et al. [72], loading the crushed fibres as 30 vol.% in a paraffin wax toroid and measured by the Nicholson and Ross technique as detailed in their paper [403]. They found that both ferrite samples had low permeabilities <2, and that BaM and SrM had $f_r$ values of 43.5 GHz and 50 GHz respectively.

7.3. CoTiM ferrites

As the MCA changes from axial to planar in BaFe$_{12-2x}$Co$_x$Ti$_x$O$_{19}$, so $f_r$ also decreases in a more-or-less linear fashion from ∼50 GHz for $x = 0$ (BaM) to <1 GHz for $x = 1$, allowing $f_r$ to be tailored over a wide range by careful substitution. For $x = 1$, $\mu' = 20$, peaking at 300 MHz, and $\mu'' = 16$ with $f_r = 500 \text{ MHz}$ [45], whereas for $x = 1.15$, $f_r = 350 \text{ MHz}$ and $\mu'' = 85$ [199], indicating that $f_r$ lowers with $x$ as $\mu''$ increases. The FMR frequency drops with increasing substitution until the anisotropy becomes planar, at $x = 1.3$ for CoTiM, at which point rotation in the plane gives the possibility of strong domain wall relaxation, raising the FMR considerably to several GHz [334]. Similarly, $f_r$ also decreases in SrFe$_{12-2x}$Co$_x$Ti$_x$O$_{19}$, from ∼50 GHz for $x = 0$ (SrM) to <1 GHz for $x = 1.5$ (Fig. 39) [404]. For BaFe$_{8.6}$Co$_{1.2}$Ti$_{2}$O$_{19}$ sintered at 970 °C, a permeability of 35 was obtained [405]. In 2 wt.% bismuth-doped BaFe$_{8.6}$Co$_{1.2}$Ti$_{2}$O$_{19}$ sintered at 950 °C/5 h, with a grain size of 40–200 nm, $f_r$ was shifted to ∼1 GHz and permeability increased from 6 to 16, with a resistivity >10$^8$ Ω cm [406].
A wide range of similar substituted ferrites have also been made using other 4+ ions and TM2+ ions, which also have an FMR range tuneable by degree of substitution. If iridium or ruthenium are used instead of titanium the material becomes planar at a much lower substitution level, therefore raising the FMR to a greater extent. In BaCo$_{1-x}$Ir$_x$Fe$_{12}$O$_{19}$ the ferrite changes to a planar anisotropy by $x = 0.4$, giving a minimum value for $f_r$ at this point. With increasing values of $x = 0.2$, 0.4, 0.6 and 0.8 the FMR frequency $f_r$ = 16 GHz, 2 GHz, 5 GHz and 7 GHz respectively, and it has a rigid canted ferrimagnetic structure that is insensitive to temperature changes [407]. When Zr$^{4+}$ was substituted instead of titanium to make BaCo$_{1-x}$Zr$_x$Fe$_{12}$O$_{19}$ ($x = 0–1.2$), it remained uniaxial up to $x = 0.6$, with $f_r > 14$ GHz, the measurement limit for this article, although $f_r$ was calculated from the anisotropy and being 28 GHz for $x = 0.4$. The measured $f_r$ was at 4.5 and 5 GHz for $x = 0.8$ and 1.2 respectively, and the $x = 0.8$ sample has also possessed the lowest coercivity [349].

7.4. Y ferrite

For Co$_2$Y, the large $H_A$ of 2228 kA m$^{-1}$ in the easy cone results in a weak FMR at $f_r = 5.7$ GHz [8]. Pure Co$_2$Y was reported as having a permeability of $\mu = 4$ and FMR at $\sim 1$ GHz, with a substantial increase in permeability up to 15 and a slight reduction in FMR frequency for $x = 0.8$, in the zinc-substituted Ba$_2$(Ni$_{1-x}$Zn$_x$)$_2$Fe$_{12}$O$_{22}$ ceramic [408]. Co$_2$Y fibres, powdered and measured as 30 vol.% in a wax toroid [403], showed a broad FMR between 6 and 7 GHz, and a possible small FMR at 1.3 GHz, with $\mu \sim 3$ below $f_r$ [75]. Pure Zn$_2$Y was reported to have a permeability of 20 below an apparent small FMR at 100 MHz, with another $f_r$ seeming to approach just above 1 GHz [409]. When Cu was substituted for Zn $\mu$ was decreased to 15 with a slight increase in $f_r$, and in Ba$_2$Zn$_{1-2x}$Co$_{2x}$Cu$_{0.8}$Y ferrite, permeability decreased and the FMR around 100 MHz disappeared with increasing Co$^{2+}$ substitution, attributed to an increase in anisotropy and a decrease in domain wall motion [409]. When sintered to 1150 °C, with a grain size >1 $\mu$m, Ni$_2$Y and Zn$_2$Y only showed single FMR peaks at $f_r = 5$ and 3 GHz respectively, but when sintered at 1300 °C the grain size increased to 4–5 $\mu$m, allowing FMR due to domain walls as well, giving diffuse peaks at 1.2 GHz in both cases, and second peaks at $f_r = 6.4$ and 3.0 GHz, respectively [410].

Both the real and imaginary parts of permittivity of Co$_{2-x}$Zn$_x$Y are reported to increase as the Zn concentration increases [398,411]. For Ba$_2$Zn$_{2(1-x)}$Co$_{0.4}$Y sintered at 1200 °C/5 h, $\mu$ was ~2 before FMR at 1 GHz, and $\varepsilon_r$ was >9 pre-FMR coming down to ~7 afterwards [398]. In a study of Ba$_2$Zn$_{2(1-x)}$Co$_{0.4}$Y it was found that as $x$ (Co content) increased from 0 to 1, permeability decreased from >10 to ~2 and $f_r$ increased from several hundred MHz to over 1 GHz [267]. Zn$_{1.2-2x}$Co$_{2x}$Cu$_{0.8}$Y ($x = 0–0.1$) showed a
clear double resonance peak at \(\sim 100\) MHz and 1 GHz for \(Zn_{1.2}Cu_{0.8}Y\), yet the lower frequency peak disappeared as Co was substituted for Zn, becoming almost unobserved even at levels as low as \(x = 0.05\). This is attributed to two mechanisms contributing to the permeability, domain wall motion and magnetisation rotation. Y ferrites with high Zn content have relatively low planar anisotropy, so domain wall motion competes with it at low frequencies, causing the lower frequency resonance. Co increases the magnetic anisotropy greatly, so the domain wall motion becomes dominated by it, and \(f_r\) moves to a higher frequency as well [362]. Not only does it seem remarkable that such a small amount of substituted Co\(^{2+}\) can have this effect, but the same paper also reports that an increase in sintering temperature of \(Zn_{1.2}Cu_{0.8}Y\) from 1025 °C to 1150 °C greatly increases permeability from 10 to 35 before these resonance features take effect, and with a simultaneous increase in the lower frequency resonance, and a reduction of the resonance frequency to <100 MHz. In this case it is attributed to an increase in grain size and reduction in porosity and grain boundaries easing domain wall motion, an effect which is increased with sintering temperature [362]. Contradictory results have recently been reported, stating that as the sintering temperature of \(Zn_{1.2}Cu_{0.8}Y\) was reduced from 1100 to 900 °C, \(\mu\) decreased from 20 to 10 below 3 GHz [405]. \(BaNi_2-xCo_{x}Fe_{16}O_{27}\) prepared at 1250 °C, where \(x = 0.8\), had very low permeability values of \(\sim 1\) at GHz frequencies, but exhibited a vague resonance and absorption effect between 32 and 40 GHz for \(x = 0.2\) and 26.5–33 GHz for \(x = 0.4\) [384].

7.5. Z ferrite

For \(Co_{2}Z\), \(H_A = 1035\) kA m\(^{-1}\) in the easy plane [8], computing to \(f_r\) between 1.3 GHz and 3.4 GHz. In early FMR studies of Co\(_2\)Z it was found that the real permeability was around 9 until it peaked at 1.1 GHz with a value of \(\mu' = 13\). The imaginary permeability peaked with a maximum value of \(\mu'' = 8\) at a FMR frequency of 1.2 GHz, in a ferrite with a density of only 4.6 g cm\(^{-3}\) (86% sintered) and a resistance of 7 \(\times\) 10\(^7\) cm. An impurity of 1% Fe\(_{2}O_3\) increased the permeabilities considerably (\(\mu' = 19\)) and resulted in a slightly denser product (4.8 g cm\(^{-3}\), 90%), but it also increased the conductivity of the sample (2 \(\times\) 10\(^7\) cm). This lowered the FMR frequency so that \(\mu'\) had a peak value of 20 at 700 MHz, and \(\mu''\) peaked at 14 at the sub-GHz frequency of 900 MHz [45].

Normally Co\(_2\)Z has FMR at 1.4 GHz, considerably lower than the calculated resonance frequency of 3.4 GHz. This is often blamed on shape and stress anisotropy, but it could also be caused by the presence of other phases, such as W, or by Fe\(^{2+}\) ions causing electron hopping to Fe\(^{3+}\) and resulting in increased conductivity. Firing in an oxygen rich atmosphere should result in less Fe\(^{2+}\) ions existing as they are oxidised to Fe\(^{3+}\), and indeed a partial pressure of only 0.1 MPa \(O_2\) was enough to produce single phase Co\(_2\)Z at 1300 °C with a higher FMR frequency of 1.8 GHz [412]. Other studies on coprecipitated Co\(_2\)Z have shown that it has an extremely narrow firing temperature stability range with Fe\(^{3+}\) converting to Fe\(^{2+}\) in extended firings, and that the cooling conditions have a great effect on FMR frequency. In a rapidly quenched from the firing temperature FMR occurred at only 700–800 MHz, in a sample cooled down at 100 °C/h this was extended to 1.5 GHz and in a sample cooled under an oxygen atmosphere \(f_r = 1.7\) GHz [199]. Very dense Co\(_2\)Z was achieved at only 890 °C/2 h with an addition of 8 wt.% PbO–B\(_2\)O\(_3\) glass, and this had a very good permeability for the sintering temperature of \(\sim 4\) at 500 MHz, an extremely high DC resistivity \(10^{10}\) \(\Omega\) cm, a specific temperature coefficient of permeability between \(-25\) °C and 100 °C \(<5 \times 10^{-6}\) °C\(^{-1}\), and a reasonable quality factor up to 800 MHz, with \(f_r > 1\) GHz [258]. Sol–gel derived Co\(_2\)Z fibres sintered to 1250 °C, powdered and dispersed as 30 vol.% in a wax toroid, where found to have a high permeability of \(>12\) below \(f_r\), and a sharp FMR occurred at 1.3 GHz [403], while the Co\(_2\)Z doped with 0.67 mol% Ca\(^{2+}\) and sintered at a lower temperature of 1200 °C had a much lower \(\mu < 5\) and a broader FMR around 1.3 Hz [75].

It has been found impossible to obtain fully dense and perfectly oriented Co\(_2\)Z, and this too has an effect of lowering the FMR frequency below the theoretical maximum. In a well oriented sample made from the coprecipitation of salts and fired to 1270 °C an FMR frequency of 1.9 GHz was achieved, and this was accredited to the material behaving as if it were a single crystal, with no domain wall contributions, because of the high anisotropy [229]. The size of the grains of Co\(_2\)Z also has an effect on the FMR of the material, due to variations in the shape demagnetising effects. It was found that the FMR frequency increased as particle size decreased, so that \(f_r = 1.0–1.2\) GHz for very large 200–600 \(\mu\)m particles, 1.1–1.3 GHz for 100 \(\mu\)m grains and 1.6–1.8 GHz for 10–25 \(\mu\)m grains [413]. It was also

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shown that in oriented Co₂Z, μ increased from 12 for unoriented to >30 for a fully oriented Co₂Z sample [414].

There was a substantial increase in permeability up to 13 and a reduction in FMR frequency to just below 1 GHz in zinc-substituted Ba₃(Co₁₋ₓZnx)₂Fe₂₄O₄₁ for x = 0.6 [408], and generally as x (Zn content) increases, so fₜ decreases and permeability increases, up to μ = 15 for CoZnZ (x = 1) sintered at 1200 °C [368]. However, when Zinc was substituted for Fe³⁺ to intentionally create a semiconductive Ba₃Co₂Fe₂₄₋ₓZnxO₄₁ ferrite, it was found that permeability decreased from 12 for x = 0 to 6 for x = 0.6 [415]. A detailed study was made by Wang et al. of Bi-doped, Cu-substituted Ba₃Co₂₋ₓCuₓFe₂₄O₄₁ sintered to over 95% density at only 900 °C. As either Bi₂O₃ content increased from 1 to 4 wt.%, or as x increased from 0 to 0.6, density and permeability increased (to maxima of 5.2 g cm⁻³ and 6.6 respectively for x = 0.6 with 4 wt.% Bi₂O₃), and resistivity and fₜ decreased with x, although they were still unusually high at 1.1–4.8 × 10⁸ Ω cm and 1.4–1.8 GHz [265]. In Co₂₋ₓCuₓZ (x = 0–0.8) sintered at 1100–1150 °C, the density increased with increasing x from 5.05 to 5.22 g cm⁻³, and the grain size was between 1 and 2 μm for all samples. Similarly permeability increased from 4.2 to 7.0 up to fₜ, which decreased from >1 GHz to ~400 MHz with x. Dielectric constant also increased with x, from 16 to 20, and remained constant up to the dielectric relaxation at <1 GHz, and the samples had high DC resistivities in the order of 10⁶ Ω cm, although it did decrease with x, attributed to the coexistence of Cu⁺ and Cu²⁺ ions [370]. When Co²⁺ and Fe³⁺ were substituted with Fe²⁺ and Cr³⁺ to make Ba₃Co₂₋ₓFe₂₄ₓ⁺yCrₓO₄₁, it was found that for values of x = 0.2 and y = 0.6, planar anisotropy had been increased, resulting in a larger Mₛ in the easy (planar) direction with a reduction in fₜ to 1 GHz and a maximum permeability of 21 [416]. Ba₃Co₀.₄Fe₂₄₀.₆O₄₁ sintered at 1300 °C has recently been reported to have μ = 30 throughout the MHz region, and with the addition of Bi₂O₃ as a sintering aid, μ = 5 could be obtained when sintered at only 950 °C, a temperature suited for multilayer LTCCs [405]. Co₂Z doped with 0.8 wt.% Nb₂O₅ and sintered at 1260 °C was found to have a very high μ of >30, but with fₜ reduced to 300 MHz, and further niobium addition decreased both μ and fₜ [417]. This was attributed to Nb⁵⁺ diffusing into the Z lattice and increasing densification and initial grain growth, but inhibiting massive DGG from occurring by forming as Nb₂O₅ on grain boundaries at 1260 °C.

A substitution of strontium for barium in Co₂Z increased the FMR from 1.4 to 2.5 GHz, [418], but substitution with lanthanum reduced fₜ [229]. Sr-substituted (Ba₁₋ₓSrₓ)₃Co₂Z (x = 0–0.8, sintered at 1250 °C/4 h, >5.1 g cm⁻³) had a very low resistivity of <10³ Ω cm, and although resistivity increased with x, fₜ remained unchanged at around 1 GHz. When SiO₂ was added (<2 wt.%) density actually decreased, but resistivity increased by two orders of magnitude (although still relatively low), and fₜ increased with increasing SiO₂ addition towards 2.5 GHz, while permeability decreased from 15 to 4.2 at 900 MHz [225]. This was attributed to the SiO₂ forming a magnetically inert, highly resistive intergranular layer, this demagnetising layer reducing permeability but increasing shape anisotropy, and therefore fₜ. Similarly, Ba₁₋ₓSrₓCo₂Z with 2 wt% PbO–Cu₂O glass sintered at 1100 °C/4 h (90% dense) had a permeability of 7–8 and fₜ of ~1 GHz [262]. The RE ion-doped iron-deficient Z ferrite systems 3(Ba₀.₅Sr₀.₅)O·2CoO·0.05Gd₂O₃·10.8Fe₂O₃ and 3(Ba₀.₅Sr₀.₅)O·2CoO·0.05Tb₂O₇·10.8Fe₂O₃, sintered to 1200 °C, had increased permeabilities as high as 15, but with fₜ reduced to ~1 GHz, and both of these features were attributed to the larger grain size of the RE doped Z ferrites. When sintered at only 1150 °C to reduce the grain size, permeability was reduced to 8 but fₜ occurred at >1.8 GHz for the Tb-doped Z ferrite [371]. The undoped, non-stoichiometric Ba₁₋ₓSrₓCo₂Fe₂₁₆O₃₇₄ sintered at 1200 °C had permeability of 2 and fₜ > 1.8 GHz, and it has also been reported that as strontium substitutes for barium in oriented Co₂Z samples permeability decreases from 18 to 6 for Sr₁Co₂Z, and that fₜ increases to ~3 GHz [226].

7.6. W ferrite

The Hₐ of Co₂W was reported as 1687 kA m⁻¹ [373], but there are few reported FMR frequencies for Co₂W, and there have been few published studies of FMR data for this material. Powdered Co₂W fibres were reported as having a broad maximum in μ' between 1 and 3 GHz as μ' decreases to half of its previous value of ~3.5, but no clear FMR peaks were observed [75,403]. Co₂W was reported as having a very low permeability of ~2 and FMR at ~3 GHz, with an increase in permeability to 7 and a reduction in FMR frequency to 1 GHz for x = 0.5, in the zinc-substituted Ba(Co₁₋ₓZnx)₁₂Fe₁₆O₂₇ ceramic [408].
7.7. U ferrite

The first reported FMR frequency of a U ferrite was in 1968, for single crystal Zn$_2$U, showing resonance between 30 and 40 GHz with a width of 16.7 kA m$^{-1}$ [23], with seemingly no investigations for 35 years afterwards, despite it being noted that they would be suitable as MW resonators in the Ka band, at 26–40 GHz, in 1969 [391]. However, recently there has been a surge of interest in the microwave properties of U ferrites, related to their excellent MW absorbing properties at higher GHz frequencies. Lisjak states on her webpage that Zn$_2$U has FMR at 30 GHz and Co$_2$U has FMR at ~1 GHz [19], and (Ba$_{1-x}$La$_x$)$_4$Co$_2$U with $x$ varying from 0.10 to 0.20, has been reported to have FMR between 9 and 11 GHz, while permeability and magnetic loss decreases with $x$, with very low values of permeability of $<0.03$ for $x = 0.2$ [249]. BaLa$_{2-x}$Co$_2$U ($x = 0.25$, $\square = $ vacancy) has a small FMR around 9.2 GHz, and equally low losses [250]. Mixed (Zn–Co)$_2$U ferrites with the formula Ba$_4$Zn$_{2-x}$Co$_x$U, where $x = 0.5–2$, were reported to have FMR between 1 and 1.3 GHz, with a small increase with increasing zinc content [240], and real and imaginary permeability increased with increasing amounts of Co [411,398]. Meena et al. have made the Ba$_4$Co$_{2-x}$Mn$_x$U ferrites, and found that $\mu'$ decreases from 0.6 at $x = 0$ to 1.5 for $x = 2$. A clear FMR was observed for Co$_2$U ($x = 0$) at 8.5 GHz, and this increased to over 9 GHz as $x$ increased to 1. However, for the samples with $x > 1$, no distinct FMR peak was seen, but rather multiple broad but small peaks between 9 and 12 GHz [247]. These blurred multiple resonances were tentatively attributed to the possible presence of undetected secondary phases, and the initial increase in $\mu$ and $f_r$ with $x$ to the higher magnetic moment of Mn$^{2+}$ ($5 \mu_B$) compared to Co$^{2+}$ ($3 \mu_B$), and higher resistance resulting in lower eddy current losses.

The same authors also measured Mn$_{2-x}$Zn$_2$U, which showed a decrease in $\mu$ with $x$, except for $x = 2$ (Zn$_2$U), which showed a very strong FMR at 11.73 GHz just after a steep increase in $\mu'$ from 1.2 to 1.6. The other sample showed multiple small but broad resonances between 8 and 12 GHz, and $x = 1$ had the largest magnetic losses [248]. Zn$_2$U also has a low temperature coefficient of resonant frequency, having a shift of <5 MHz between −55 to +85 °C (=35 kHz/°C = 1.3 ppm/°C at 26 GHz) [391]. In a study of Ba$_2$Zn$_{2-x}$Co$_x$U with $x = 0–2$ sintered at 1200 °C, Haijun et al. reported that while permittivity was ~11 for all samples except $x = 2$ (Co$_2$U, which had $\varepsilon_r \sim 16$ at 100 MHz, dropping towards 11 at GHz frequencies), permeability was ~1.3 for Co$_2$U, 2.1 for Zn$_2$U and peaked at ~3.7 for $x = 1.5$, and $f_r$ increased from 609 MHz for Zn$_2$U ($x = 0$) to 1.32 GHz for $x = 1.5$, with no FMR observed at all for Co$_2$U [420]. These FMR values reported for pure Zn$_2$U from the mixed (Zn–Co)$_2$U studies are clearly very different from the high values reported for standard ceramic samples, for reasons which have never been explained. As P$^{5+}$ was substituted into Ba$_4$(Co$_{1-x}$P$_{2x}$)U ($x = 0–0.2$), FMR shifted to a higher frequency and then disappeared altogether at $x = 0.2$, although the magnetic losses ($\mu''$) were extremely low [250].

7.8. X ferrite

Ba$_4$Zn$_{2-x}$Fe$_{28}$O$_{46}$ hexaferrites with $x = 2; 0.16, 1.2; 0.8, 0.4$ and 0.0 prepared by the citrate sol-gel process showed a small decrease in $f_r$ with an increase in Zn content, low permeability values between 2 and 3.5, and a generally poor FMR response around 1 GHz. For Co$_2$X $f_r = 1.2$ GHz with a permeability of ~2.5, and for Zn$_2$X $f_r = 0.7$ GHz with a permeability of ~3.6 [421]. In a follow-up paper, the same authors give permittivity values of ~10 and a dielectric resonance at 4.8 GHz for all values of $x$ sintered at 1200 °C. They also give sub-GHz permeabilities of ~2 for Zn$_2$X, ~3 for Co$_2$X and ~5.5 for $x = 0.8$, and $f_r$ values rising from 728 MHz for Zn$_2$X to 1.20 GHz for Co$_2$X, with $f_r = 968$ MHz for $x = 0.8$ [241]. In this latter sample, $x = 0.8$, they also noticed a second resonance peak at around...
4 GHz, which was unexplained, and in the samples fired to 1100 °C, which contained BaM as an impurity phase, the fᵢ values were slightly higher, due to the increased anisotropy contribution of the M ferrite.

8. Magneto-electric (ME), multiferroic (MF) and dielectric properties of hexaferrites

8.1. Dielectric properties

The dielectric properties as well as magnetic properties are very important for many high frequency applications of hexaferrites, particularly if they are to become integrated chip components. The key properties of interest for many applications are resistivity and permittivity (dielectric constant, ε, or relative permittivity, εᵣ; a measure of how easy it is to establish, or “permit”, an electric flux in a material), which in general should both be as high as possible at as higher frequency as possible. As with permeability, a complex permittivity can be measured consisting of real (ε’(ω)) and imaginary (ε”(ω)) components, from which dielectric resonance and losses can be calculated. The metal cations and the oxygen anions form dipoles, creating an intrinsic dielectric polarisation. The dominant conduction mechanism in ferrites is electron hopping between Fe²⁺ and Fe³⁺.

Well sintered samples of BaM, SrM and CaM (the later doped with 4 mol% La₂O₃) were found to have εᵣ of ~10, ~20 and ~15 respectively when measured at 10 GHz, and the Cu₂Z substituted versions had similar values, with εᵣ decreasing slightly as x increases. Interestingly, from the measurements of ε’ and ε”, CaCo₂Ti₆Fe₁₂₋₂ₓO₁₉ (with 4 mol% La₂O₃) seemed to show a clear dielectric resonance at 10 GHz for x = 0.8 and 8.75 GHz for x = 1 [175].

Pure Co₂Z has a dielectric constant of <20, resistivity of 1–2 × 10⁷ Ω cm, and consequently high dielectric losses of tan δ~ 0.2 up to 1 GHz. By comparison, Cu substituted Z ferrite, Ba₃Co₂ZₓCu₂₋ₓFe₂₄O₄₁ where x = 0.05–0.25 sintered at 1120 °C, had permittivity of ~25–30 and dielectric losses an order of magnitude lower, even up to 1 GHz. This was attributed by Zhang et al. to the conductivity being half of that of the pure Co₂Z, the Cu²⁺ reducing Fe²⁺ formation and lowering sintering temperature (Fe⁳⁺ → Fe²⁺ + e⁻ is a high temperature process), and to the Cu²⁺ creating internal stresses that reduce electron hopping [422]. Therefore, maintaining a low conductivity is a key property in improving the dielectric properties of hexaferrites. Similarly, the dielectric constant at low (MHz) frequencies was shown to be greatly increased when Mn³⁺ was substituted for iron atoms in Ba₃Co₂₋ₓMnₓO₄₁, as manganese reduces the amount of Fe²⁺ ion present in a buffering reaction where Mn³⁺ + Fe²⁺ → Mn²⁺ + Fe³⁺ [423]. Ba₃Co₁.₆₋ₓZnxCu₀.₄Fe₂₄O₄₁ had a permittivity of 31 (at 400 MHz) and a resistivity of ~3.5 × 10⁷ Ω cm for x = 0.15 when sintered at 1125 °C/4 h [369].

In a study of the effects of cation deficiency on the formation of the Y phase, it was seen that for Ba₂Zn₁ₓCo₀.₉–ₓFe₁₂₋ₓO₂₂₋₁.₅x, resistivity reduced with temperature at a much lower rate in the deficient ferrites (x = 0.5–1) than in the stoichiometric Y ferrite (x = 0) [214]. This was assumed to be because cation deficiency will restrain the variation of charge on Fe ions, and any deficiencies will tend to gather at grain boundaries, where they form a more resistive surface, further impeding conduction. A higher degree of sintering will reduce amount of grain boundaries (reducing this insulating effect), and the higher temperatures usually required for greater sintering will also increase Fe²⁺ formation. It was higher degree of sintering will reduce amount of grain boundaries (reducing this insulating effect), and gather at grain boundaries, where they form a more resistive surface, further impeding conduction. A cause cation deficiency will restrain the variation of charge on Fe ions, and any deficiencies will tend to gather at grain boundaries, where they form a more resistive surface, further impeding conduction. A higher degree of sintering will reduce amount of grain boundaries (reducing this insulating effect), and the higher temperatures usually required for greater sintering will also increase Fe²⁺ formation. It was higher degree of sintering will reduce amount of grain boundaries (reducing this insulating effect), and gather at grain boundaries, where they form a more resistive surface, further impeding conduction. A cause cation deficiency will restrain the variation of charge on Fe ions, and any deficiencies will tend to
However, for $x = 1-1.5$, small and broad multiple resonance peaks were observed, increasing in size with $x$, and for $x = 2$ (Mn$_2$U) a very sharp dielectric resonance peak was clearly seen at 11.8 GHz (Fig. 40a and b) [247]. This indicates a much lower dielectric loss, and hence greater resistivity, in Mn$_2$U, and is a feature rarely seen in ferrites, which tend to be relatively conductive compared to many good dielectric ceramics. Furthermore, this peak also coincides almost exactly with the small FMR peak seen in Mn$_2$U by the same authors at 11.9 GHz, suggesting the possibility of coupling between these two properties. The same authors measured Mn$_{2-x}$Zn$_x$U, and all samples showed multiple broad resonance peaks between 8 and 12 GHz, except for $x = 1$, which also had a larger grain size >20 μm and much higher magnetic losses [248]. As seen in their other paper, the pure Mn$_2$U had a very sharp dielectric resonance at 11.89 GHz, with a pre-resonance $\varepsilon'$ of ~15, indicating low dielectric losses (Fig. 40c and d). Interestingly, $x = 2$ (Zn$_2$U) had an even stronger, but broader, dielectric resonance at 11.75 GHz, with a pre-resonance $\varepsilon'$ ~17, and the $x = 1.5$ sample had a sharp, but smaller, resonance around 11.3 GHz, and a lower $\varepsilon$ (Fig. 40c and d). Once again, these peaks coincide with peaks in FMR, small for $x = 0$ and 1.5, but a much stronger FMR at 11.73 GHz for the pure Zn$_2$U, suggesting coupling of these two strong resonances. $\varepsilon'$ of ~15 was reported for Zn$_{2-x}$Co$_x$U, with a slight dielectric resonance ~4.4 GHz [398]. The same reference gives a lower $\varepsilon'$ of ~13 for Zn$_{2-x}$Co$_x$W, and no dielectric resonance between 0.1 and 6 GHz. In lanthanum-substituted (Ba$_{1-3x}$La$_{2x}$)$_4$Co$_2$U ($x = 0$, 0.15 and 0.2), partial substitution of Ba$^{2+}$ by La$^{3+}$ increased $\varepsilon'$, but increased $\varepsilon''$ to a greater extent, the increased electron hopping from La$^{3+}$ ions raising the dielectric loss [249]. A similar effect was seen in P$^{3+}$ substituted Ba$_4$(Co$_{1.5}$P$_{2.5}$)$_2$U ($x = 0-0.2$) [250].

It has been reported that BST aids sintering of Z ferrites, increasing density, but also promotes the formation of BaM as a minor phase impurity [424]. The effect of a Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) additive on the complex permeability and permittivity of Co$_{0.4}$Zn$_{0.6}$Z was investigated in the range of 1 MHz-1 GHz.
BST is a dielectric perovskite used in many electronic applications at MW frequencies, e.g. as a capacitor or frequency filter, and it has a very high $\varepsilon_r$ of $\sim 1000$ [425]. At levels of 0.1–1.5 wt.% both permeability and permittivity were improved, but the BST also encourages grain growth. This paper appears to report $\varepsilon > 100$ (as opposed to $\sim 10$ for Co$_2$Z) and $\mu$ as high as 35 at hundreds of MHz, and a decrease of the $f_r$ to $< 1$ GHz. However, none of these samples appear to be pure phase Z ferrite, with either a coexistence of the Y phase, or the higher levels of BST forming BaM and perovskite impurity phases, which will have strongly affected the magnetic and dielectric properties, especially at higher frequencies. Therefore, these results are not at all easy to interpret [426].

8.2. Magnetoelectric (ME) and multiferroic (MF) properties

ME materials provide coupled magnetic and electrical phenomena. That is, a magnetic field affects the electrical polarisation, and an electrical field affects the magnetisation. This can also affect non-ferroic properties such as permittivity, permeability or resonant frequencies, and can be via a direct stimulus due to an applied field, or an indirect stimulus through the application of voltage or stress. MF materials have direct coupling between their ferroic properties (exhibiting reversible hysteresis in an applied field), such as ferromagnetism, ferroelectricity, and/or ferroelasticity. ME and MF properties often overlap, but not all ME materials are necessarily MF.

There has been an explosion of interest in such materials in recent years [427–429], as they have a multitude of potential applications, such as:

- Dual field read-write magnetic memories and data storage.
- Sensors and switches, transducers, active responsive materials and components.
- Controlled or adaptive absorption and resonance of EM fields from RF to MW and GHz.
- Field-tuneable MW components such as filters, oscillators, phase shifters and duplexers.

However, to date much research has concentrated on single phase (MF) materials: a single material that has both ferromagnetic and ferroelectric properties, with direct coupling between them. Unfortunately, single phase MF materials are inherently very difficult to produce [430]. This is because the conditions that lead to good ferromagnetic properties are opposed to those that lead to good ferroelectric properties. The factors that create magnetisation (aligned spin of electrons) and dielectric properties (polarisation of atoms) do not tend to coexist. In most cases, single phase ME/MF materials exhibit useful properties only at very low temperatures (<50 K), or very high applied fields (>1 T).

Another possibility is to study two phase ME/MF materials. In this case, a product property concept is used, where the combined materials have a property (the ME coefficient, $\alpha$, from ME coupling) which does not exist in the individual materials. Therefore, there has been increasing interest in recent years in ME coupling in composite materials composed of magnetostrictive and piezoelectric phases. Such systems show strong ME interactions that are orders of magnitude stronger than in single phase ME materials [431]. ME coupling can be caused either by magnetic or electric fields. The magnetic phase of a composite subjected to a magnetic field adjusts its geometry to minimise anisotropy energy (magnetostriction), and this will cause a strain that affects the polarisation of the ferroelectric phase due to piezoelectricity, which can generate a current. In case of an electric field as a stimulus, a reverse piezoelectric effect and an inverse magnetostriction (Villari effect) are responsible for ME output. Thus, ME coupling is a product property of magnetostrictive and piezoelectric phases of the composite. Commonly the ME effect is quantified in two ways:

$$ ME = \frac{\text{electrical}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}} $$

units of $\alpha = V \text{ cm}^{-1} \text{ Oe}^{-1}$

$$ ME_{II} = \frac{\text{mechanical}}{\text{electrical}} \times \frac{\text{magnetic}}{\text{mechanical}} $$

units of $\alpha_{II} = \text{Oe cm V}^{-1}$

Here the ME effect is when an electric field is applied, and ME$_{II}$ is when a magnetic field is applied. CGS units are still commonly used for $\alpha$, although strictly speaking the SI units are $s m^{-1}$, where
1 mV cm\(^{-1}\) Oe\(^{-1}\) = 5.54 ps m\(^{-1}\). More details on the complex measurement of these ME coefficients can be found in work by the UK National Physical Laboratory and Oakland University [432].

Much work has been done on thin film composites, where strain effects between two nanolayers of ferromagnetic and ferroelectric materials can demonstrate indirect ME coupling. However, direct coupling measurements have proved problematic in such materials, and fully reversible MF phenomena are found to be rare. Poor stoichiometry control and lattice mismatch inducing strain further complicate thin films. The alternative is bulk composites, where both direct and indirect coupling phenomena may coexist depending on the type of composite and intimate mixing at the micro or nanolevel. Bulk composites could include thick films, tapes and bilayers, particulate-solution based coating, fibres or nanoself-assembly.

8.2.1. Composite ME materials

The synergistic property effect of a composite ME material is determined by the properties of the two phases and the interaction between them. This was first suggested by Philips Laboratories in 1948 [433], but it wasn’t until 1972 that Philips Laboratories grew the first ME composites from a eutectic mix of ferroelectric barium titanate (BaTiO\(_3\), BT) and magnetic CoFe\(_2\)O\(_4\) [434]. Depending on the growth conditions, ME coefficients of up to \(\alpha = 130\) mV cm\(^{-1}\) Oe\(^{-1}\) (720 ps m\(^{-1}\)) were obtained, exceeding the largest values seen in single phase ME compounds by at least an order of magnitude in even these early experiments. However, these were still much lower than theoretical models, which predicted of \(\alpha\) values 1–2 orders of magnitude higher [427]. This was attributed to several causes: reactions between constituents or interdiffusion, the low resistivity (and eddy currents) of the magnetic phase, mechanical/physical defects in the interface between the constituents (pores or micro-cracks from lattice strain), and difficulties in aligning the dipoles to maximise the piezoelectric response. Also, in layered bulk composites, \(\alpha\) increases with an increasing thickness ratio between the magnetic and piezoelectric layer, while the output voltage (extremely important for sensor applications) decreases, and in multilayer composites \(\alpha\) can decrease greatly with an increasing number of layers [427]. Despite this, Srinivasan et al. made PZT/NiFe\(_2\)O\(_4\) thick films by tape casting (\(\geq 10\) \(\mu\)m), with measured \(\alpha\) up to 1.5 V cm\(^{-1}\) Oe\(^{-1}\) after sintering as multilayer stacks, partly because the lattice of NiFe\(_2\)O\(_4\) nearly matches that of PZT, reducing inter-layer strain [435]. They also found that transverse ME effects perpendicular to the layers were up to ten times higher than longitudinal ME effects parallel to the layers, a feature common to all layered composites.

There are various ways in which the components can connect in a ME composite, but the most common are the 0–3 type (typically magnetic particles in a piezoelectric matrix, to improve resistivity), the 2–2 type (stacked alternating layers) and the 1–3 type (aligned fibres of one phase embedded in another), as shown in Fig. 41a–c. Various theoretical modelling has predicted that as the aspect ratio of the fibre in a 1–3 type 50%–50% CoFe\(_2\)O\(_4\) fibre – BT matrix composite increases, the ME coefficient, \(\alpha\), will also increase for aspect ratios of up to 100 (Fig. 41d) [436]. However, to the author’s knowledge, no such structures have yet been prepared with ferrites, although as we show in Section 9, the ability to make high quality aligned hexaferrite fibres already exists. Whether a 0–3 or 1–3 type, the problems of conductivity, porosity and poor homogeneity on a micro- or nanoscale greatly reduce the optimum \(\alpha\) values. Despite this, NiFe\(_2\)O\(_4\)-PZT 0–3 composites, sintered at 1250 °C with 10–20% ferrite, have shown \(\alpha = 115\) mV cm\(^{-1}\) Oe\(^{-1}\), due to their homogenous microstructure and high density [437].

Resonance ME effects are also very important, so that if the resonance frequencies overlap (dielectric, magneto-/electromechanical or FMR) there will be a coupling that will greatly enhance the ME effect around that frequency. Experiments at such resonance frequencies with PZT/Permendur alloy composites have produced massive ME coefficients as high as \(\alpha = 90\) V cm\(^{-1}\) Oe\(^{-1}\) at \(\leq 400\) kHz (10\(^3\) higher than at low frequency) [438], and \(\xi_{\parallel} = 1–5\) Oe cm kV\(^{-1}\) in PZT/YIG composites at 9.3 GHz [439]. This is still very dependent upon density, however – as porosity increases from 5% to 40%, the ME effect can decrease by >95% at high resonance (FMR) frequencies [436]. Hot pressing and spark plasma sintering (SPS) are methods to greatly increase density of composites (to over 99%), using relatively lower temperatures and sintering times of only a few minutes in the case of SPS, and this increases coupling. Homogeneity can be improved by mixing the components with wet chemical processing (sol–gel, co-precipitation), ideally using the piezoelectric phase as the sol–gel or co-precipitated phase around a dispersed ferrite particulate, to increase resistivity in the finished composite.
A ME composite made of CoFe$_2$O$_4$ NPs dispersed in a BT sol–gel made core@shell NPs, preventing conduction between the ferrite grains and maintaining a well dispersed ferrite phase, and this showed a $d_{33}$ piezoelectric coefficient 6 times higher, and $z$ three times larger, than samples that were just milled together [440].

There have been several investigations of bulk ceramic composites containing M ferrite and BT. The component ferroic phases are well known for their excellent magnetic and piezoelectric properties respectively. Pure BT exhibits peaks in $e_r$ at 398, 273 and 183 K as it changes from cubic $\rightarrow$ tetragonal $\rightarrow$ orthorhombic $\rightarrow$ rhombohedral, with the largest peak in $e_r$ around $T_c$ of 398 K when it changes from paraelectric (cubic) to ferroelectric (tetragonal) [425]. Although this effect is greatly reduced in the composites, peaks can clearly be seen in the plots at all frequencies around 400 K ($T_c$ of BT) indicating that the composites have still retained a degree of ferroelectricity. This allows for the possibility of some kind of ME coupling by applying a voltage to the dielectric, or changing permittivity by applying a magnetic field.

Srinivasan et al. have investigated BaM – lead zirconium titanate (PZT) bilayer single crystal heterostructures, which exhibited FMR at 50 GHz under a field of 0.6 T, with a narrow peak width of 1 MHz with a quality factor of 50,000. This peak could be tuned to slightly higher frequencies with the application of a voltage (a shift of +8 MHz with 10 kV cm$^{-1}$), and an increase in absorption [441]. This represented a ME coupling ($\delta E/\delta E$) of 0.8 MHz cm kV$^{-1}$. However, this was much smaller than the calculated ME coupling coefficient of 22 MHz cm kV$^{-1}$, and only represented a total shift of 80 ppm of the 50 GHz frequency. This ME coupling was strain-mediated by the piezoelectricity of the PZT. Aluminium substituted M ferrite-PZT bilayers were also investigated, using BaAl$_2$Fe$_{10}$O$_{19}$ single crystals. These showed FMR at ~100 GHz, and exhibited a similar tuneability of $-8/+6$ MHz with an applied voltage of $-1/+8$ kV cm$^{-1}$, albeit with a higher applied field of ~1 T [442]. The same team have also recently investigated SrM, SrAl$_{0.8}$Fe$_{11.2}$O$_{19}$ and SrAl$_{1.2}$Fe$_{10.8}$O$_{19}$ – PZT bilayer composites, and found that while with SrM there is almost no induced ME voltage with magnetic field, with increasing Al$^{3+}$ substitution the ME coupling increases greatly, at reasonably low fields of 0.2 T, giving induced ME voltages of $>2.5$ mV for SrAl$_{1.2}$Fe$_{10.8}$O$_{19}$ [443]. This resulted in a ME coupling coefficient of
8 mV cm$^{-1}$ Oe$^{-1}$ for both AC and DC magnetic fields. They also found that unlike the other bilayers, these samples all showed a linear ME response in both AC and DC magnetic fields, as long as these fields were applied in the plane of the uniaxial M ferrite crystal. This could allow the development of dual AC/DC magnetic field sensors.

Srinivas et al. have recently reported BaM-BT composite ceramics made from mixed powders sintered at 1300 °C/5 h. These were made with varying ratios of BaM:BT, and there was no indication of the phases reacting. As the ferrite content increased the conductivity increased, polarization decreased, $M_s$ increased, and $H_c$ decreased slightly, and the ferroelectric hysteresis loop also became more well defined. ME coupling was measured, and although it decreased greatly with increasing BaM, for 25% BaM-75% BT the ME output was 1.45 mV with fields between 0.6 and 10 T [444]. The ME output vs. applied field was non-linear, and showed a hysteresis when the field was reversed (Fig. 42a). The authors claim that this non-linear ME effect is evidence of a MF property with composition up to 40% BaM via a piezoelectrically-induced polarization, at room temperature, but with a large (>0.5 T) applied magnetic field. $P$ was 3.48 and 2.54 μC cm$^{-2}$, with a remnant polarization of 0.59 and 0.39, and coercive electrical fields of 4.47 and 2.35 kV cm$^{-1}$, for the ferroelectric hysteresis loops of the 20% and 40% BaM compositions, respectively [445].

BaM-BT composite ceramics were also investigated by Karpinsky et al. [446,447], who experienced similar problems with the conductivity increasing greatly in BaM-rich composites. They studied the samples by PFM and MFM, and showed the piezoelectric hysteresis loops of the composites (Fig. 42b), although greatly reduced compared to pure BaM, were still evident, and measured a greatly decreased peak in $\varepsilon'_e$ around the $\varepsilon'_c$ of BT at 400 K in 10% BaM samples. The $M_s$ of BaM was diluted as expected by BT, with little effect on $H_c$. They demonstrated that an electrical field of 25 V applied over an area of 2 μm$^2$ resulted in a change in the magnetic phase map obtained by MFM. This presented a magnetic domain wall movement of 100 nm, around the domain size of BaM, a stress mediated effect from the piezoelectric–magnetic coupling of the BaM-BT, and yielded a low ME coupling coefficient of 0.1 mV cm$^{-1}$ Oe$^{-1}$ for the 50% BaM sample. Subsequent work by the authors on BaM-BT and SrM-BT ME composites is on-going, and has shown MFM evidence of changes in the magnetic properties of a BaM grain when a voltage is applied locally to a specific neighbouring piezoelectric grain (Fig. 42c), proving there is local nanoscale ME coupling between the two. These experiments were all carried out, and ME coupling demonstrated, at room temperature and with no applied magnetic fields required.

In studies on Co$_2$Z ferrite sintered in air at high temperature (1300 °C/6 h) to encourage oxygen deficiency as Fe$^{3+}$ → Fe$^{2+}$, it was found the Z ferrite can become semiconducting with a very high metal-like $\varepsilon'_e$ of >1500 below the dielectric resonance that occurs at 200 MHz, beyond which permittivity turns negative due to its high conductivity. A substitution of Fe$^{3+}$ by Zn$^{2+}$ increased conductivity, $\varepsilon'_e$ and the degree of dielectric resonance (still at 200 MHz), as Zn$^{3+}$ formed preferentially at some iron sites, increasing the amount of Fe$^{2+}$ and hence its semiconductor. When combined with YIG (yttrium iron garnet) in a two-slab composite material (YIG having a negative permeability around the FMR frequency, which can be increased from 2.9 and 3.9 GHz by applying an increasing magnetic bias), a potentially very interesting left-handed material with both negative permeability and permittivity was produced between 2.7 and 3.7 GHz, when a field of 42–67 kA m$^{-1}$ was applied [415]. Such left-handed materials have potential applications in novel MW and optical devices, and more interest in similar meta materials (e.g., negative refractive index materials) based on hexaferites is sure to develop in the future. A two slab composite of Co$_2$Z-PMN-PT (lead magnesium niobate-lead titanate, PbMg$_{0.33}$Nb$_{0.67}$O$_3$-PbTiO$_3$, a mixed perovskite ferroelectric/piezoelectric) has also been made. With an applied electrical field of 6 kV cm$^{-1}$, it exhibited a permeability change of 16%, measured from an induced magnetic field of 0.0038 T, giving a tuneability of 2.7% per kV cm$^{-1}$. This should induce a similar magnitude change in the FMR frequency, although this was not demonstrated in the article. However, it was shown that when the electric field was applied to the PMN-PT slab there was a small increase in the FMR line width of <2.6%, and a decrease in FMR field from 0.084 to 0.080 T, showing that there was piezoelectric-magnetostrictive ME coupling between the two slabs. This was calculated to equal an FMR tuneability of 41.6 MHz/kV cm$^{-1}$ [448].
8.2.2. Single phase ME and MF hexaferrites

Two Y ferrites and a Z ferrite initially raised great interest recently as single phase MF/ME ceramics, and other M, Y and U ferrites have since been reported as being MF. They all seem to have electrical polarisation induced by a magnetic field, in some cases up to RT, attributed to their helicoidal/spiral non-collinear magnetic spin structures. This seems to occur mainly in strontium containing hexaferrites, but arises from the “magnetic spin frustration” of competing magnetic interactions (the various

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**Fig. 42.** (a) ME output vs. applied magnetic field for (B) 25% BaM–75% BT, (C) 50% BaM–50% BT and (D) 75% BaM–25% BT composites by Srinivas et al. [444]. (b) Piezoelectric hysteresis loops of BT, 90%BT–10% BaM and 50% BT–50% BaM composites measured by PFM by Karpinsky et al. [447]. (c) MFM images showing change in magnetic phase before and after a neighbouring BT grain was locally poled with 90 V, 700 nm from the grain boundary with BaM. The black and red signals show the change induced in magnetic order by poling, measured along the lines on the MFM images. Previously unpublished results by D.V. Karpinsky, R.C. Pullar and A.L. Kholkin.

8.2.2. Single phase ME and MF hexaferrites

Two Y ferrites and a Z ferrite initially raised great interest recently as single phase MF/ME ceramics, and other M, Y and U ferrites have since been reported as being MF. They all seem to have electrical polarisation induced by a magnetic field, in some cases up to RT, attributed to their helicoidal/spiral non-collinear magnetic spin structures. This seems to occur mainly in strontium containing hexaferrites, but arises from the “magnetic spin frustration” of competing magnetic interactions (the various
magnetic superexchange interactions), which are present in all hexaferrites. This long-range helical magnetic ordering occurs in other types of crystal as well, but so far the hexaferrites are unique in that this can occur at RT, and the review by Kimura gives more details of these non-collinear spiral magnets [449]. Note that these materials may not strictly be ferroelectric (and therefore are not strictly MF), although a MF phase plays a key role in the magnetic-field induced polarisation – it may be better thought of as a ME response driven by phase competition. They could be called “spin-driven ferroelectrics”. The direction of the induced polarisation can be switched through a magnetoelectric annealing procedure, an effect suggesting a potential application as an unusual non-volatile, low-power memory device. If such an effect can be achieved at low applied fields, this behaviour could be potentially used as either a magnetically rewritable ferroelectric memory, or an electrically rewritable magnetic memory.

The first hexagonal ferrite that was discovered, by Kimura et al. in 2005, to be a single phase MF material was single crystal $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ ferrite [360]. This was previously described by Momozawa et al. as consisting of alternate layers of two kinds of magnetic spin blocks, the S block which contains barium and iron tetrahedra, while the L block contains no barium and zinc tetrahedra. However, ordering normally occurs in which an amount of iron and zinc swap tetrahedral sites, to give $\text{Fe}Zn_{1-x}$ in the S block and $Zn\text{Fe}_{1-x}$ in the L block. The standard physical structure S and T blocks of Y ferrite are indicated on the right of the structure [451].

![Fig. 43. The $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ structure, showing the iron and zinc polyhedra and the sites of the large barium cations (black spheres). The arrows indicate directions and magnitude of parallel spins in the collinear ferromagnetic structure. The magnetic S and L blocks are shown on the left of the structure. The S block contains the barium irons and iron tetrahedra, while the L block contains no barium and zinc tetrahedra. However, ordering normally occurs in which an amount of iron and zinc swap tetrahedral sites, to give $\text{Fe}Zn_{1-x}$ in the S block and $Zn\text{Fe}_{1-x}$ in the L block. The standard physical structure S and T blocks of Y ferrite are indicated on the right of the structure [451].](image-url)
The exchange interaction between the S and L blocks is weak and, as a consequence, the relative directions of the total spins of the blocks change with the external magnetic field and with temperature, leading to a complex magnetic phase diagram. The B–T magnetic phase diagram between 8 K and 300 K derived by Kimura et al. [360] is shown in Fig. 44b, and the magnetic spin structures for each phase proposed by Momozawa et al. [450] are shown in Fig. 44c. It is important to note that the helical, intermediate II and III, and collinear phases are all obtainable at room temperature.

Of course, this in itself would not make BSZY a MF material, but Kimura et al. reported a clear hysteretic relationship between changes in magnetisation, magnetocapacitance (Δe), ME current (J_ME) and electrical polarisation (P) with a change in applied magnetic field B (Fig. 45) [360]. This was particularly apparent for the phase changes between the intermediate II–III phases at 0.3 T (large peaks in Δe and J_ME) and the intermediate III-collinear phases at 2.2 T (smaller peaks in Δe and J_ME), and a very large peak in P of 150 μC m⁻² for the intermediate III phase (at ~1 T, 10 K). Furthermore, after poling with E = 220 kV m⁻¹ to measure P, the polarisation was retained even in the absence of an applied electrical field E, and the sign of P could be reversed by poling an opposite E, thus demonstrating a ferroelectric-like switchable polarity when a magnetic field B = 0.3–2.2 T was also applied, and the intermediate III phase was present. These properties were also measured with temperature, and while in general they decreased with increasing temperature, Δe showed a maximum at 50 K and P at 30 K, and the field B at which the peaks occurred increased with temperature, requiring B = 1 T at 130 K to induce the ferroelectric-like intermediate III phase.

Although it can be seen in the magnetic phase diagram that the intermediate III phase should be present at room temperature at applied fields of B = 0.8–1.2 T, spontaneous P was measureable only up to 110 K. Above this temperature conductivity became too great to permit poling by E, but magnetocapacitive measurements showed that the ferroelectric-like phase can exist up to over 300 K. BSZY also displayed an additional type of ME coupling, magnetically rotatable ferroelectric polarisation.

Fig. 44. (a) Schematic crystal structure of Ba₀.₅Sr₁.₅Zn₂Fe₁₂O₂₂, where S and L refer magnetic structure blocks of the Y ferrite. The pink lines show weak antiferromagnetic coupling between Fe(4) and Fe(5) via superexchange, and the inset box shows competing strong and weak superexchange mechanisms. (b) Magnetic phase diagram. Grey area corresponds to phase boundaries. Field B applied perpendicular to the c-axis. (c) Proposed models for the evolution of magnetic structures by applying B perpendicular to the c-axis [450]. The long and short arrows indicate μ_L and μ_S, respectively. The numbers below each model corresponds to those of the magnetic phases in (b). X represents the Néel temperature of 326 K. Reproduced from Kimura et al. [360].
The direction of $P$ was perpendicular to both $B$ and the $c$-axis, and the polarisation could be rotated continuously in the hexagonal plane by changing the direction of $B$. This was also demonstrated by rotating $B$ (1.1 T) through $30^\circ$ steps in the plane, starting with it perpendicular to $E$ (which was also in the plane), where $P$ had a maximum value of $150 \, \mu\text{C m}^{-2}$. As $B$ was through $90^\circ$ so it was parallel to $E$ in the plane, $P$ was reduced to zero, and changed to $-150 \, \mu\text{C m}^{-2}$ when at $180^\circ$ to $E$ [360]. This continuous rotation of $P$ using $B$ provides the interesting possibility of novel devices based on a magnetically controlled electro-optical response, analogous with liquid crystals where the polarisation direction is controlled by $E$.

*Ab initio*–calculated exchange interactions showed that the magnetism in BSZY is highly sensitive to the Fe and Zn ion distributions, and as a result the region of existence of the non-collinear spin structures, and hence of ferroelectricity, is rather narrow. Iron ions completely occupy four octahedral sublattices, while two tetrahedral sublattices $6cT$ and $6cS$ are filled partially by zinc and partially by iron (Fig. 43). The fraction of Fe in the $6cT$ sublattice is equal to the fraction of Zn in the sublattice $6cS$, and the required value of this fraction, $\gamma$, for the non-collinear phases to exist is $0.44–0.62$ [451]. This is around $\gamma = 0.5$, which corresponds to a random distribution of Fe and Zn, and if such control could be achieved, the authors suggest that ferroelectricity may be found not only for a single concentration of strontium, but in a much broader class of hexaferrite compounds. Chai et al. have reported that the room temperature resistivity of BSZY single crystals increased by more than three orders of magnitude (to $10^5 \, \Omega \text{cm}$) upon being subjected to an optimised heat treatment, that included

![Fig. 45.](image-url)
post-growth annealing in a flowing O\textsubscript{2} atmosphere at 900 °C/8 days, followed by slow cooling at a rate of 50 °C/h \[452\]. This was attributed to the removal of oxygen deficiencies, and for ordering to achieve a γ value of 0.661. This reduced conductivity allowed them to measure Δε and P to over 300 K, and they were able to chart the ferroelectric phase diagram as well as the magnetic phase diagram up to the Néel temperature. While their magnetic phase boundary broadly matched that of Kimura et al., they were surprised to find that the ferroelectric phase diagram did not match it at all at higher temperatures – the low field ferroelectric phase boundary moved abruptly toward \(B = 0.01\) T at ~280 K and remained there up to 310 K, until it disappeared above 315 K. This was assumed to be the helical spin ordering Néel temperature, above which the ferroelectric phase ceases to exist.

This was an unexpected finding that the ferroelectric phase required very small applied magnetic fields of only 0.01 T to exist above 270 K. Below 220 K, the magnetic and ferroelectric phases boundaries virtually coincide, even in the as-grown crystal regardless of heat treatment, but the phase boundaries of intermediate III clearly deviate above 220 K and in the low-B regions, suggesting that the ferroelectric phase becomes independent of the intermediate III phase near the spin ordering temperature. The authors suggest that the ferroelectric phase in BSZY can be associated with a canted or transverse conical spin configuration. At temperatures below 220 K, the intermediate III phase seems to almost coincide with this canted conical phase. However, as the temperature increases, the spin anisotropy required to confine the spin moments within the plane will be naturally weakened. In such a situation, it is highly likely that the canted conical spin structure starts to appear at a much lower B than the intermediate-III phase, explaining why the phase boundaries separate. This remarkable result showed that in a resistive ferrite a single phase MF material could be obtained at room temperature with a very small applied field of only 0.01 T.

Polycrystalline BSZY ceramics where made by Kamba et al. from a citrate gel, calcined at 1100 °C and sintered at 1100 °C/72 h in air. They found that subsequent slow cooling at 6 °C/h between 1100 and 900 °C, followed by cooling to room temperature in 90 min, produced a ceramic with conductivity several orders of magnitude lower than rapidly cooled polycrystalline samples or annealed and slowly cooled single crystals \[453\]. This was attributed to reduced oxygen deficiency. Despite this, the ceramics were still more conductive than the O\textsubscript{2} annealed sample of Chai et al., and their electrical properties could not be measured above 250 K. Consequently, their phase diagrams resembled those of Kimura et al., the polycrystalline ceramics requiring a field of ~0.5 T near zero K and ~1 T at 250 K to induce the intermediate III phase. The permittivity of the slow cooled ceramic increased greatly above 100 K as metal-like conduction occurs, but this occurred at only 50 K for the other samples.

It was also found that if aluminium is substituted for iron, the ME properties of Ba\(_{0.5}\)Sr\(_{1.5}\)Zn\(_2\)Fe\(_{12-x}\)Al\(_x\)O\(_{22}\) single crystals can be efficiently tailored by the Al-substitution level. As \(x\)
increases, the critical magnetic field for switching electric polarisation is systematically reduced down to an extremely small 10 mT (100 G), and the ME susceptibility is greatly enhanced to reach a giant value of $2 \times 10^5$ ps m$^{-1}$ at an optimum $x = 0.08$ [454]. It is suggested that this giant magnetoelectricity occurs because the Al substitution progressively stabilises a longitudinal heliconical state, as opposed to the helical spin phase seen in unsubstituted BSZY (Fig. 46). This has recently been confirmed for $x = 0.08$, where a small amount of substitution by Al$^{3+}$ reduces anisotropy to the benefit of ME properties, but more than 8% substitution causes too much loss of anisotropy [455]. The stabilisation of this ferroelectric phase at near-zero magnetic field is one of the most important steps for the application of these type of MF materials, and this was the first single phase MF material that could switched at room temperature by a small magnetic field. Nickel has also been substituted for zinc to make Ba$_{2-x}$Sr$_x$Ni$_2$Y single crystals, and it was found that for $x = 1.5$, and to a lesser extent for $x = 1.25$, when a magnetic field was applied in the hexagonal plane a non-collinear ME intermediate state existed between 10 and 250 K for $x = 1.5$. A large ME induced polarisation of 160 $\mu$C m$^{-2}$ was measured at 30 K for $x = 1.5$ at a field of 0.3 T, but although the ME intermediate phase existed until 250 K, ME effects could not be measured above 100 K, as resistivity became too high. By annealing the samples at 900 °C/8 days and then cooling under O$_2$ at a rate of 50 °C/h, a more resistive sample was made which had measurable ME induced polarisation up to 175 K [456].

In 2008 the coexistence of ferroelectric polarisation and spontaneous magnetisation was reported in Ba$_2$Mg$_2$Y, at zero applied magnetic field and below ~200 K, by Taniguchi et al. [457]. There was also a MF effect, as the reversal of magnetisation by a small magnetic field <0.02 T was accompanied by an electric polarisation reversal, through the clamping of ferrimagnetic and ferroelectric domain walls. This was attributed to a change from the collinear spin ferrimagnetic state ($T_c = 553$ K) to a non-collinear helical–spiral spin structure below 195 K, in which the spins rotate around the c-axis (the $S_m$ and $L_m$ blocks in Fig. 47a), in a similar manner to BSZY. As can be seen in the Fig. 47c and d, both magnetisation and polarisation exhibited stepped hysteresis loops indicating competing phase transitions with applied

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**Fig. 47.** (a) Crystal structure of Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$ projected along the b axis. Large green and small red spheres represent Ba$^{2+}$ and O$^{2-}$ respectively. Fe$^{3+}$ and Mg$^{2+}$ are randomly distributed in octahedral and tetrahedral sites. $L_m$ and $S_m$ are magnetic blocks, in which magnetic moments of Fe$^{3+}$ are collinearly aligned. (b) Temperature dependence of magnetisation along the b axis at 0.01 T in a field cooling (FC) process. (c and d) Magnetic field dependence of magnetisation (M) and electric polarisation (P) at 4.3 K in magnetic fields parallel to the b axis, respectively. In this figure the applied field B is labelled $\mu_H$. The inset of (c) shows the M around a magnetic field of H = 0 T. P is parallel to the a’ axis. Blue closed circles in (c) represent M measured in the first B-sweep after zero-field cooling (ZFC). $P_s$ is measured in E = 0 after poling by applying an electric field of E = 460 kV m$^{-1}$ [457].
magnetic field, and there is a small $M_z$, and significant $P (\sim 25 \, \mu\text{C} \, \text{m}^{-2})$ at zero field ($B = 0$). $P$ increased to a sizeable $100 \, \mu\text{C} \, \text{m}^{-2}$ with $B = 0.02 \, \text{T}$ at 4.3 K. It was shown that the ferroelectric-like switch in polarisation occurs in the plane of the crystal, perpendicular to the $c$-axis about which the helical magnetisation is oriented, and it was suggested that the change in magnetisation character around $0.13 \, \text{T}$ was due to a switch from the helical $c$-axis magnetisation to the direction of the applied field, as seen with BSZY [457]. However, unlike in BSZY (in which no spontaneous polarisation appeared at $B = 0$), this indicated that the magnetic-field-induced ferroelectric-like phase of BSZY is stabilized at zero magnetic field by the substitution of Mg$^{2+}$ for Zn$^{2+}$. Not only can $P$ be reversed by low $B < 0.02 \, \text{T}$, but it was also possible to perform a sequential flipping of $P$ by scanning $B$ in the low field range, giving a reversible and reproducible variation of $P$ without noticeable decay in its magnitude over many cycles at 4.3 K [457]. This could lead to a ferroelectric memory that can be magnetically recorded, though the low resistivity of their sample prevented measurement of this polarisation flip above 30 K. Taniguchi et al. also demonstrated that $P$ could be reversed from 100 to $100 \, \mu\text{C} \, \text{m}^{-2}$ by rotating $B$ through $180^\circ$, as with BSZY, and a field of only 0.25 T was sufficient to achieve full reversal (at 4.3 K) [457].

Ferroelectric-like behaviour was also reported by Ishiwata et al. in 2008 at almost the same time, also in single crystals of Ba$_2$Mg$_2$Y under a very low applied field of 30 mT (300 G), below 195 K [458]. They constructed a complex $B$–$T$ magnetic phase diagram for Ba$_2$Mg$_2$Y from 5 to 160 K, and $B$ up to 4 T (Fig. 48), and identified several magnetic phase transitions. It is collinear ferrimagnetic below 553 K, and adopts a non-collinear proper helical screw spin structure in the plane below 195 K (Fig. 49b). The angle between moments on adjacent blocks is about $70^\circ$ at 9 K. They also found a spin-reorientation transition to a longitudinal conical state at around 50 K (Fig. 49c), still with zero applied field, which showed up as the onset of a spontaneous magnetisation along the [001] direction, which continued to increase with decreasing temperature. In addition to the proper helical screw state (and the longitudinal conical state below about 50 K) at $B = 0$, there are four other kinds of magnetic phases which develop with any applied field. Unexpectedly, three of them (FE1, FE2, and FE3 in Fig. 49) are ferroelectric phases, and the other one (PE in Fig. 49) is a paraelectric phase, these phases being distinguishable by observed plateaus in the magnetisation curve, with magnetisation increasing as the phases develop with increasing applied field, $B$ (at 5 K below):

<table>
<thead>
<tr>
<th>Magnetic State</th>
<th>Field Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal conical (at 5 K)</td>
<td>$B = 0 , \text{T}$</td>
</tr>
<tr>
<td>FE1 transverse conical</td>
<td>$0 , \text{T} &lt; B &lt; 60 , \text{mT}$</td>
</tr>
<tr>
<td>FE2 unknown structure</td>
<td>$60 , \text{mT} &lt; B &lt; 0.12 , \text{T}$</td>
</tr>
<tr>
<td>FE3 non-collinear ferrimagnetic</td>
<td>$0.12 , \text{T} &lt; B &lt; 3.8 , \text{T}$</td>
</tr>
<tr>
<td>PE collinear ferrimagnetic</td>
<td>$B &gt; 3.8 , \text{T}$</td>
</tr>
</tbody>
</table>
The polarisation, $P$, increased linearly from low values at $B \sim 0$ to $20 \mu C m^{-2}$ for the FE1 phase, then increased again linearly but much more rapidly from $20$ to $\sim 65 \mu C m^{-2}$ during the FE2 phase, before forming a plateau of $80 \mu C m^{-2}$ for most the FE3 phase, and collapsing to zero at the onset of the non-ferroelectric PE phase [458]. Interestingly, they did not claim to have measured a polarisation at zero field and $5 K$, suggesting that the longitudinal conical phase is not ferroelectric, but as soon any field was applied the ferroelectric FE1 phase developed. With further neutron diffraction studies it was found that the unidentified FE2 phase region actually consisted of three heliconical phases, and that at least two magnetic phases are able to coexist at fields below $0.5 T$ [459]. In Zn substituted single crystals of $Ba_2(Mg_{1-x}Zn_x)Y$ also investigated by Ishitawa et al., the anisotropy can be controlled, with field and $x$ dependent ME responses – as $x$ increases, the field-induced polarisation decreases rapidly to near zero at $x \sim 0.3$, $M_s$ increases, and there is a change in magnetic anisotropy from conical to planar at $x = 0.66$, above which the collinear ferromagnetic structure dominates at all temperatures, as it also does in field of $>5 T$ for all values of $x$ [460].

The third hexaferrite that was identified as a MF material is the Z ferrite $Sr_2Co_2Fe_{24}O_{41}$, or $Sr_3Co_2Z$ (SCZ). This ferrite was first reported and characterised by Pullar et al., who noted a strange 2-step room temperature magnetic hysteresis loop (Fig. 37), for a very soft but highly magnetic ferrite [224]. This non-monotonic, but graded or step increase in the magnetisation curve, up to a saturation magnetic field, suggested that it is not a simple ferrimagnet at room temperature. The shape of the magnetisation curve is actually very similar to that of BSZY, and this drove Kitagawa, Kimura and co-workers to investigate the potential ferroelectricity of SCZ in 2010 [366]. As they expected, SCZ had a similar helical–spiral magnetic ordered state and a resultant magnetoelectric effect at room temperature, as the Z structure contains the same structural components as the Y ferrite. A recent article has demonstrated that the helical spin effect arises in SCZ through the same process as in the ME Y ferrites: That is, in terms of the magnetic superexchange between two Fe sites crossing the boundary between the L and S layers [461]. The Ba ions are near these two sites, and when Ba is substituted by Sr this changes the Fe–O–Fe bond angle through this boundary, i.e. from $113^\circ$ in $Zn_2Y$ to $118^\circ$ in BSZY. This causes the magnetic frustration which stabilises the helical spin states. In Co$_2Z$ this angle = $116^\circ$, but in SCZ it is $123^\circ$. Therefore, this angle is $5^\circ$ larger in SCZ than in BSZY, and it is suggested that this may enhance the magnetic frustration, stabilise it to higher temperatures, and increase its ME performance.

Fig. 49. (A) Schematic crystal structure of $Ba_2Mg_2Y$. The magnetic structure consists of alternate stacks of L blocks (brown) and S blocks (green) having large and small effective magnetic moments, respectively ($\mu_L$ 2.8 times greater than $\mu_S$). Illustrations of helicoidal spins (represented by arrows) (B) with proper helical screw ($50 < T < 195 K$), (C) longitudinal conical ($T < 50 K$), and (D) slanted conical ($T < 195 K$ and $B \sim 30 mT$) spin structures [458].
Kitagawa et al. made polycrystalline SCZ ceramics with standard ceramic techniques using stoichiometric oxides, calcined at 1000 °C/16 h, isostatically pressed and sintered in air or O2 at 1200 °C/16 h, and then cooled slowly at 60 °C/h. SCZ sintered in oxygen exhibited a low-field magnetoelectric effect at room temperature, with an applied field of 0.2–0.3 T, despite the fact it seemed not to be a pure Z phase, with some U and W ferrite present. This was because the O2 sintered SCZ had a resistivity of 1.3 × 108 Ω cm, enormously greater than the air sintered SCZ with a resistivity of only 6 × 105 Ω cm. A low P of only 10 μC m−2 was measured at 300 K, peaking at B = 0.25 T, during the phase in which the magnetisation curve increases more slowly with increasing field, between B = 0.1–0.7 T. Even at zero applied field (B = 0), a small degree of polarisation remained at room temperature, and εr ~ 16.7. The ME current also showed sharp peaks at these two values of 0.1 and 0.7 T even at room temperature, as a magnetic phase change occurs, with maximum values of 4 μA m−2 at 300 K, compared to 10 μA m−2 for BSZY at 10 K. At 1 T SCZ became a pure ferrimagnet, but an applied field of 0.03 T was enough to see a strong ME effect. The measured ME coefficient, α, exceeded 1 × 10−10 s m−1 below 0.04 T, and reached a maximum of 2.5 × 10−10 s m−1 with a very small applied field of only 30 mT. The value of αmax was more than 50 times larger than the coefficient of a linear ME effect in Cr2O3. In the air sintered ceramic, a similar effect was seen, but only below 150 K, due to its greatly increased conductivity. These authors also carried out a sequential switching of the electric polariisation by oscillating the magnetic field B between 0 and 0.25 T at 300 K, with out any signs of decay between cycles [366]. The sign of the ME signal can be determined by the sign of the polarity of the switching electrical field, and the state of the system was maintained in the absence of any applied electrical or magnetic field, showing promise for applications such as non-volatile memories controlled and detected by an electrical field.

High frequency ME measurements have also been carried out on SCZ. On a polycrystalline sample that was quenched after sintering to prevent formation of M, W or Y phases, and then annealed in O2 at 600 °C/6 h to increase resistivity (to 1.43 × 109 Ω cm), measurements where carried out up to 4 GHz. When an electric field of 5 kV cm−1 was applied parallel to the direction of magnetisation, there was an increase of permeability from about 3.75 to 5.15 at low frequencies, but by 0.5 GHz the change in μr was minimal, and with no change above 2 GHz. When an electric field was applied perpendicular to the magnetisation, a reduction in μr occurred of a similar magnitude [462]. This means that it would seem that electrical tuning of the broad FMR peak observed between 3 and 4 GHz is not possible, although non-ME magnetic tuneability would be expected. SCZ was also shown to have an electrostriction of 7 ppm strain with an applied field of 10 kC cm−1, and showed a more-or-less linear strain response to applied electric field. It has also been shown by RT time domain THz spectroscopy of polycrystalline SCZ, that applying a magnetic field of only 0.1 T parallel to the polarising incident THz wave increased THz absorption over the 1.3–6 THz range, with a particular increase around 5 THz [463]. Applying a magnetic field perpendicular to the incident THz wave had the opposite effect, lowering the degree of THz absorption. An even greater effect (up to 200% increase) was seen with fields of 0.2 T applied to Ba2Mg2Y, but only at low temperatures and over a narrower THz range [464]. This effect, known as terahertz magnetochromism, demonstrates that potentially many hexaferrites with non-collinearly ordered spins may exhibit such THz frequency resonance, irrespective of the presence or absence of spontaneous electrical polarisation.

Given its structural similarity to Z ferrite, it is no great surprise that Sr4Co2U ferrite has also very recently been reported as a RT ME material. It also has a cone of magnetisation at RT, and is a very soft magnet. Highly resistive samples were made by sintering a sample in O2 at 1150 °C, and then post-annealing this at 1000 °C and cooling it down slowly over 24 h, all under O2 to avoid Fe2+ formation. This gave a ceramic with a high resistivity of ~4 GΩ cm at RT. The electric polarisation was measured with a magnetic field of 3 T and a perpendicular field of 0.4 MV m−1, and the magnetic field swept at 1 T min−1. There was almost no polarisation at zero T, but a rapid rise to 0.2 μC m−2 (at RT) at a field of 0.2–0.3 T, and a decrease back to zero at fields >0.8 T, when the magnetisation becomes almost saturated and the magnetic hysteresis loop closes. Although two orders of magnitude less than the ME effect seen in Sr3Co2Z, at −73 °C the maximum induced polarisation is increased to >0.5 μC m−2 at 0.3–0.4 T [34]. Furthermore, this induced polarisation was close to zero at 80 °C, at which temperature the magnetic moment begins to rotate towards uniaxial anisotropy. This shows that there may be many more ME and MF hexaferrites.
yet to be discovered, with the same ME mechanism, based on non-collinear spins in ferrites with conical anisotropy.

An M ferrite has also been found to be ME/MF by Tokunaga et al., and it has different behaviour due to its uniaxial anisotropy. The MF compositions investigated were BaFe$_{11.95-\alpha}$Sc$_\alpha$Mg$_{0.05}$O$_{19}$, because scandium substituted BaM has already been seen to have longitudinal conical spin structures from neutron diffraction at 77 K. Values of $\alpha$ between 1.6 and 1.8 were chosen, and a substitution of 0.05 Mg$^{2+}$ was included to reduce conductivity by inhibiting Fe$^{2+}$ formation. The samples were made as single crystals [465]. The magnetic structure can be viewed as consisting of two blocks, R and R$^\prime$ (Fig. 50a) With no applied magnetic field, the helical spins aligned along the c-axis, and the spins align collinearly within each block, but interblock coupling is noncollinear (Fig. 50b). The half cone angle $\alpha$ is 30° for $\alpha = 1.8$. However, if a magnetic field is applied at an angle to the c-axis, the spins can exist canted in a cone at an angle to the axis (Fig. 50c), called the tilted state, and if a field is applied perpendicular to the axis, the cones can be perpendicular to the axis (Fig. 50d), called the transverse state. In all cases, the interblock coupling is non-collinear.

At higher temperatures up to the Curie temperature, the M ferrite has a normal ferrimagnetic structure. However, below a certain temperature, the non-collinear helical spin states in Fig. 50b–d appear. For $\alpha = 1.6$, the ferrimagnetic state undergoes a transition to the non-collinear states below 270 K, with an associated loss in magnetisation, and the loss is much greater when the magnetic field is aligned perpendicular to the c-axis, due to the formation of these transverse helical spins. The maximum transition temperature is 370 K for $\alpha = 1.75$, so this non-collinear magnetic ordering can exist at room temperature. Unfortunately, the low resistivity of the $\alpha = 1.75$ compound ($3 \times 10^2 \Omega$ cm at RT) meant that its ME properties could not be measured and poling was difficult, so all ME measurements were carried out on the $\alpha = 1.6$ compound. The magnetic (H) and electrical fields were applied at 90° to each other, and both in the plane perpendicular to the c-axis. The initial magnetisation curves and H induced polarisation are shown in Fig. 50e and f, and it can be seen that at first polarisation increases with H to a maximum, and then decreases to near zero as the magnet saturates. The peak in polarisation can also be seen as a dramatic change in the magnetisation curve, e.g. at 0.5 T at 5 K, and both the magnitude of, and H required for, peak polarisation decreases with increasing temperature. In this transverse state, the polarisability is not reversible – once it is lost, it never recovers, and a virtually zero polarisation is seen when H is reversed to zero in all cases (Fig. 50f). Above 250 K no polarisation can be induced for $\alpha = 1.6$, suggesting that the transverse conical state is less stable than that in the ME

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**Fig. 50.** (a) The crystal structure and magnetic R and R$^\prime$ blocks, (b) aligned helical non-collinear spin structure in zero magnetic field (H), and the (c) tilted and (d) transverse non-collinear spin structures when H is at 45° and 90° to the c-axis, respectively, for BaFe$_{11.95-\alpha}$Sc$_\alpha$Mg$_{0.05}$O$_{19}$ ($\alpha = 1.6–1.8$). (e and f) show the initial magnetisation (M–H) and curves and induced polarisation (P–H), when H is at 90° to the c-axis, for $\alpha = 1.6$. (g) the helical spin state phase diagram [465].
Y ferrites, due to their strongly uniaxial anisotropy. A helical spin state phase diagram is shown in Fig. 50g. However, when $H$ is applied at 45° causing the tilted state, not only does the polarisation not decrease all the way to zero, maintaining a value even up to $H = 1.4$ T at 5 K, but upon reversal of the field there is still a polarisation, albeit somewhat reduced. Most strangely, between 20 and 30 K the direction of the polarisation changes from positive to negative. This can be seen in Fig. 51, where $M$–$H$ and $P$–$H$ curves are shown at 10 and 30 K, with $H$ at 45° to form the tilted state. It can be seen that at 10 K $P$ goes from positive to negative in a hysteresis loop, while at 30 K it forms a butterfly loop, always positive. The was explained as being because at 10 K the domain wall has a transverse conical structure, and the spiral plane rotates with $M$. At 30 K, the domain wall has a proper screw structure and never rotates, instead becoming “squashed” and then increasing again, but always positive. This effect has not been seen in the other, hexaplana, MF hexaferrites.

9. Hexaferrite composites

9.1. Multiphase ceramic composites

To lower the coercivity of BaM while maintaining the high saturation magnetisation for use in magnetic recording applications, composite ferrites have been made, in which BaM is coated with 36 wt.% nanocrystalline superparamagnetic particles of iron oxide, which have zero coercivity. The original M ferrite had a coercivity of 271 kA m$^{-1}$ and $M_s = 70.3$ A m$^{-2}$ kg$^{-1}$, and after particles of $\delta$-FeOOH ($M_s = 19.7$ e A m$^{-2}$ kg$^{-1}$) were added to the surface the composite had an $H_c$ of 182 kA m$^{-1}$ but a much lower $M_s$ of 45.5 A m$^{-2}$ kg$^{-1}$ [466]. More successful was a coating of superparamagnetic magnetite particles ($M_s = 62.2$ A m$^{-2}$ kg$^{-1}$) which gave a composite with $H_c = 117$ kA m$^{-1}$ and $M_s = 58.9$ A m$^{-2}$ kg$^{-1}$ [467]. In both cases there must be magnetic coupling interactions between the two components, as the composite values are less than the simple sum of the component values. It was also found that in BaM with 36% magnetite the anisotropy had been moved to a preferred magnetisation in a cone.
at an angle of 22° to the c-axis. This could be restored by using a mixed spinel Co₉Fe₃−₀.₁O₄ to make the composite with x > 0.25, and if x = 1 then Mₛ was increased to 65 A m⁻² kg⁻¹ [468].

A composite BaM/α-Fe material was made by reducing 100 nm sized BaM, with Hc = 334 kA m⁻¹ and Mₛ = 50.2 A m² kg⁻¹. After reduction at 380 °C/4 h the coercivity had dropped to 39 kA m⁻¹ but the Mₛ increased greatly to 97.2 A m² kg⁻¹, due to the formation by reduction of α-iron. The paramagnetic effects of the α-iron also interfered with the superexchange interactions of the ferrite, changing the magnetic anisotropy from uniaxial to planar, moving through a cone at an angle to the c-axis at lower reduction temperatures [469].

Mixed BaM/spinel ferrite compounds were also made from the glass crystallisation method at 800 °C, using the spinels CoFe₂O₄, NiFe₂O₄, ZnFe₂O₄, Co₁₋ₓZnₓFe₂O₄ and Ni₁₋ₓZnₓFe₂O₄. All of these were found to increase Mₛ except NiFe₂O₄, and usually the higher the Mₛ of the spinel the higher the Mₛ of the composite. NiFe₂O₄ has a lower Mₛ than BaM, and the sum of the compounds gave a lower net Mₛ for this material. The non-magnetic ZnFe₂O₄ was the exception, as the zinc ion prefers the tetrahedral sites in the M structure to such an extent that they displaced Fe³⁺, raising Mₛ as a result. The coercivity was also raised with increasing spinel addition, especially in the case of the very hard CoFe₂O₄ [470]. The incomplete hydrothermal decomposition of BaM with a strong reducing agent resulted in the decomposition of some of the BaM to Fe₂O₄ to form a composite with stacked single-domain plates of the two ferrites, intergrown on a nanoscale [471]. The combination of their soft and hard magnetic properties could be tuned by varying relative composition, with potential applications as magnetic hyperthermia biomedical materials.

Mixed ceramic phase composites of 20% Ni₀.₆Zn₀.₂Cu₀.₂Fe₂O₄ spinel ferrite in Co₂Z were made, where the two ferrites remained as discrete phases when sintered at 1020 °C/4 h with a density of 4.75 g cm⁻³ [472]. This composite had a high permeability of up to 9 and FMR at around 1 GHz, despite the low sintering temperature. An in situ composite composed of ceria-stabilized tetragonal zirconia polycrystals (Ce-TZP) and La(Co₀.₅Fe₀.₅(Fe₀.₉Al₀.₁)₁₁)O₁₉ was synthesised from a powder mixture of Ce-TZP, La(Fe₀.₉Al₀.₁)O₃, Fe₂O₃, Al₂O₃, and CoO [473]. The dense Ce-TZP dispersed with plate-like La(Co₀.₅Fe₀.₅(Fe₀.₉Al₀.₁)₁₁)O₁₉ crystals as a second phase were formed after sintering from 1250° to 1350°C. The saturation magnetisation of the in situ composite Ce-TZP/La(Co₀.₅Fe₀.₅(Fe₀.₉Al₀.₁)₁₁)O₁₉ was proportional to the mass fraction of the hexaferrite second phase in Ce-TZP. The coercivity of the composite with a 20 mass% of second phase decreased from 728 to 201 kA m⁻¹ after the pulverisation of the composite.

Although not exactly composites, highly porous BaM foams have been made, with the aim of filling the 0.5–1 mm pores with another material (semi- or superconductors, polymers, etc.) to form a hybrid structure. Unfilled foams are also light weight, and have low thermal expansion and conductivity. The foams were made using the replication technique, in which a 50% porous polyurethane foam was filled with a slurry of oxides as a template, and then removed by pyrolysis in air (650 °C). Foam replicas were made using the replication technique, in which a 50% porous polyurethane foam was filled with a slurry of oxides as a template, and then removed by pyrolysis in air (650 °C). Foam replicas were then sintered at a very high temperature of 1400 °C/2 h, and compact samples made at the same temperature for comparison [474]. Pure BaM phase was made, and the sample consisted of very large grains, many around 10 µm, although apparently with no decomposition of the BaM phase (Fig. 52 d). Foams were made with 30 and 80 pores in.−¹, and the pores were all interconnected, with few cracks in the struts. In the foam with 30 pores in.−¹, the pores were 0.5–1 mm wide, with a porosity of 90 vol.%, and the grains were of a similar size to the compact (Fig. 52a and b). In the foam with 80 pores in.−¹, the pores were 0.1–0.3 mm wide, and it had a porosity of 85 vol.% [475]. The magnetisation loops of the foams and the compact are shown in Fig. 52f, and if can be seen that they all had quite high Mₛ values of 63 and 55 A m² kg⁻¹ for the compact and foams respectively, but low Hc and Mₛ values due to the large grain growth in all samples. The two foams were almost identical, with Hc = 64 kA m⁻¹, slightly larger than the compact due to the open structure hindering superexchange coupling. Foams were also made at the slightly lower temperature of 1300 °C using a B₂O₃ sintering aid, and Hc was increased to 167 kA m⁻¹ with 0.5 wt.% B₂O₃ [476].

9.2. Ferrite-polymer composites

Ferrite-polymer composites have their attractions, as apart from ease of manufacture and forming into shapes, the polymer can reduce dielectric loss, especially at low frequencies, while having little effect on MW absorption and FMR. Polyvinylidene fluoride (PVDF (−CH₂CF₂−), ε = 5 at 10 MHz) is a
particularly interesting polymer, as it is a thermoplastic that is also piezoelectric, with a piezoelectric coefficient as large as 6–7 $\text{pC N}^{-1}$, 10 times larger than that observed in any other polymer [477]. Electric polarisation in the order of 100 mC m$^{-2}$ has been seen in polyvinylidene fluoride-trifluoroethylene copolymer (PVDF-TrFE) films. Co$_2$Z/polymer composites were made by adding the ferrite to PVDF, using variously sized Co$_2$Z particles between 10 and 150 $\mu$m, and the volume fraction was varied between 0 and 1 (i.e., 100% ferrite). For 0.7Z/0.3PVDF composites permittivity was increased to 30–40 at

Fig. 52. SEM images of BaM foams sintered at 1400°C/2 h with (a and b) 30 pores in$^{-1}$ and (c) 80 pores in$^{-1}$, and (d) the sintered BaM compact [474,475]. (e) Photograph of a 4 cm block of the sintered BaM foam [474]. (f) Magnetisation curves for the compact and foams sintered at 1400°C [475].
The composite. The 43% Co$\text{Z}_2$ composite had low magnetic losses of 0.0085 at 100 MHz, rising to 0.077 at 1 GHz, compared to 0.6 for the pure Co$\text{Z}_2$ at only 100 MHz. Complex permittivity and dielectric spray-dried oxides, sintered at 1150 °C, mixed with a 1/3 or 2/3 volume ratio with polyethylene, and flame sprayed to make the composites. $M_r$ decreased with composition as would be expected, and $H_c$ remained high in the composites, up to 190 and 318 kA m$^{-1}$ for the BaM and SrM composites, respectively. $\varepsilon_r$ was ~3 and $\mu_r$ ~1 for all composites, and $f_t$ was around 45 and 50 GHz for the BaM-2/3 and SrM-2/3 coatings, with an absorption of >80% for BaM-2/3 below 50 GHz.

Composites of Co$\text{Z}_2$ in a modified polypropylene (ER182) matrix were measured up to 1 GHz with volume fractions between 20.6 and 43%. Although only measured from 10 MHz to 1 GHz, below the FMR $f_t$ of Co$\text{Z}_2$, it could be seen that $\mu'$ was rising towards a resonance at 1 GHz. The permeability was low (1.35–1.5) in the composites at lower frequencies, compared to 12 for the bulk ceramic, but $\mu'$ was approaching 2 at 1 GHz, and as expected it increased with increasing ferrite content in the composite. The 43% Co$\text{Z}_2$ composite had low magnetic losses of 0.0085 at 100 MHz, rising to 0.077 at 1 GHz, compared to 0.6 for the pure Co$\text{Z}_2$ at only 100 MHz. Complex permittivity and dielectric loss increased with increasing Co$\text{Z}_2$ content, and decreased with frequency, with no resonance seen in the permittivity spectra. The measured values for the various Co$\text{Z}_2$-polymer composites are shown in Table 14 [480].

Polyaniline (PANI, –C$_6$H$_4$–NH–C$_6$H$_4$–NH–) is a crystalline conducting polymer, which also has excellent environmental stability (about as reactive as silver), simple synthesis, and controllable conduction through variation of the oxidation state via doping. PANI is also ferromagnetic, with a low $M_s = 5.3$ A m$^2$ kg$^{-1}$ and a reasonably hard magnetic $H_c = 153$ kA m$^{-1}$ [481]. This obviously makes it a very interesting polymer for making hexaferrite composites. BaM NPs were reacted with PANI in a one step process, to make PANI-coated BaM particles around 200 nm diameter. As the amount of PANI increased relative to BaM, the $M_r$ reduced as expected, but the reflection losses of the PANI-BaM composites could be tuned between 7 and 16 GHz by varying the thickness of the PANI layer [482]. 300 nm SrM and SrFe$_{12-2x}$(ZnZr)$_x$O$_{19}$ particles have been coated with PANI shells to make composite particles of about 0.5–1 μm diameter. Their magnetic properties were dominated by the M ferrite cores, so although $M_s$ decreases greatly with PANI content, the composites maintain a hard magnetic nature [483]. BaM-BT/PANI composite materials have also been made, based on 50:50 wt.% mixtures of BaM and BT. It was shown that the composite had electronic transition and interaction between the ceramics and PANI components, and that the PANI affected the MW absorption of the ceramics, lowering the frequencies slightly of the absorption peaks, and increasing the degree of absorption compared to just the mixed ceramics, at around 8 and 32 GHz. However, the most interesting result was that the composite material masked the detection of heat signatures on IR thermal imaging. A plate coated with various materials was placed in front of a black body at a point where the temperature was 1000 °C, and the thermal image was taken at mid-wave IR (3.5 μm) and long-wave IR (8–12 μm). As can be seen in Fig. 53, the PANI and individual ceramics, while better than polyethylene, had little effect on the heat signature, whereas both the mixed ceramics by themselves, and the ceramic/PANI composite, had a great effect, lowering both peak and average temperature signals considerably [484]. The effect was slightly better for the composite than for the mixed ceramics. This was due to an ME effect from the mixed ceramics and the composite dissipating the IR energy, and give rise to the possibility of simultaneous MW and thermal shielding and stealth capabilities in such ME materials.

### Table 14

<table>
<thead>
<tr>
<th>Vol% Co$\text{Z}_2$</th>
<th>$\varepsilon_r$</th>
<th>Tan $\delta_e$</th>
<th>$\mu_r$</th>
<th>Tan $\delta_m$</th>
<th>$\varepsilon_r/\mu_r$</th>
<th>1/($\mu_r\varepsilon_r$)$^{1/2}$</th>
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<td>20.6%</td>
<td>5.41</td>
<td>0.056</td>
<td>1.58</td>
<td>0.059</td>
<td>3.42</td>
<td>0.34</td>
</tr>
<tr>
<td>28.2%</td>
<td>6.68</td>
<td>0.075</td>
<td>1.67</td>
<td>0.066</td>
<td>4.00</td>
<td>0.30</td>
</tr>
<tr>
<td>35.7%</td>
<td>8.42</td>
<td>0.093</td>
<td>1.77</td>
<td>0.072</td>
<td>4.74</td>
<td>0.26</td>
</tr>
<tr>
<td>43.0%</td>
<td>10.95</td>
<td>0.159</td>
<td>1.80</td>
<td>0.077</td>
<td>6.09</td>
<td>0.23</td>
</tr>
<tr>
<td>0 (pure ER182)</td>
<td>2.41</td>
<td>0.0002</td>
<td>1.06</td>
<td>n/a</td>
<td>2.27</td>
<td>0.65</td>
</tr>
</tbody>
</table>

~ 1 GHz and permeability was 3–5 at 100 MHz with FMR occurring >1 GHz, with the lower values being for the smaller sized ferrite particles [478]. SrM and BaM composites with polyethylene have been prepared by Lisjak et al., from stoichiometric spray-dried oxides, sintered at 1150 °C, mixed with a 1/3 or 2/3 volume ratio with polyethylene, and flame sprayed to make the composites. $M_r$ decreased with composition as would be expected, and $H_c$ remained high in the composites, up to 190 and 318 kA m$^{-1}$ for the BaM and SrM composites, respectively.

Changes in $\varepsilon_r$, dielectric loss (tan $\delta_e$), $\mu_r$, magnetic loss (tan $\delta_m$), ratio of $\varepsilon_r/\mu_r$ and miniaturisation factor (1/($\mu_r\varepsilon_r$)$^{1/2}$) for polypropylene ER182-Co$\text{Z}_2$ composites [480].
9.3. Carbon nanotube (CNT) – hexaferrite composites

The first report to combine CNTs with hexaferrite to enhance the magnetic properties of the hexaferrites was by Shakirzianov et al. in 2009 [485]. They showed that a composite of 70% Sc-doped BaM in a dielectric polymer with a small amount of CNTs absorbed at between $-8$ to $-15$ dB over a frequency range of 10–23 GHz, and the CNTs also increased the attenuation bandwidth. SrM coated MWCNTs were made in 2010 by firstly treating the MWCNTs in nitric acid to modify their surface, and then mixed with nitrates (Fe: Sr = 11.5) and combusted via a citrate route. The obtained powders were then calcined at 850 °C/2 h, and the single phase SrM particles were 10–30 nm in diameter. With higher concentrations of MWCNTs the SrM formed along the nanotubes, and as this increased the 1D aligned nature of the SrM, it also increased $H_c$ slightly in the material [486]. No values were given for the amounts of CNT used in this work. When CNT-BaM composites with different doping ratios were investigated between 2 and 18 GHz, it was found that the microwave absorption properties of the composite improved with increasing amounts of CNT. When CNTs were 6 vol.%, the maximum reflection loss of a 3 mm sample reached 30.8 dB at 10.5 GHz [487].

Ghasemi et al. have published several articles on hexaferrites-CNT nanocomposites since 2010. MWCNTs were added to BaFe$_9$Mn$_{0.5}$Co$_{0.75}$Ti$_{1.5}$O$_{19}$ NPs previously made by a sol–gel process as 2, 3 and 4 vol.% of the ferrite. Not surprisingly, the CNT decreased the $M_s$ of the ferrite, both due to volume dilution and induced surface strain effects. However, there was also a large effect on the MW absorption of the ferrite. The pure ferrite showed a $-20$ dB absorption bandwidth between 16.5 and 19 GHz, with two definite resonance peaks around 17 and 19 GHz, of $-37$ and $-42$ dB, respectively [488]. As the amount of CNT increased, the overall absorbance improved between 16 and 19 GHz, and the frequency of these two peaks decreased slightly, but their magnitude increased greatly, to $-56$ dB with 4 vol.% CNT (Fig. 54a). This occurs because of a match between the dielectric losses from the CNT and the magnetic losses from the ferrite. Similar nanocomposites were made with BaFe$_9$Mg$_{0.5}$Co$_{0.75}$Ti$_{1.5}$O$_{19}$ NPs produced from a reverse micelle process (10–15 nm), mixed with 1–5 vol.% CNTs. These showed a similar decrease in $M_s$ with increasing level of CNT, but also a significant reduction in $H_c$ with increasing CNT content, which was not satisfactorily explained by the authors (Fig. 54b). These Mg substituted M ferrites also showed resonance at lower frequencies of 9–11.5 GHz, again with two peaks around 9.5 and 11.5 GHz, but much lower absorbance of $<10$ dB for the pure ferrite up to peak values $<-40$ dB with 5 vol.% CNT [489]. A TEM image of these nanocomposites is shown in Fig. 54c. Ghasemi has also reported MWCNTs coated with thin films of SrFe$_{12-2x}$(Cr$_{0.5}$Al$_{0.5}$)$_x$O$_{19}$ [490] and SrFe$_{12-2x}$(Zn$_{0.5}$Sn$_{0.5}$)$_x$O$_{19}$ [491], also made from a sol–gel process, to give a uniform ferrite layer.
30 nm thick (Fig. 54d). These showed similar trends in magnetic and MW behaviour to the nanocomposites.

SrM/MWCNT/PANI composites were made from citrate-gel-derived SrM sintered at 900 °C/4 h, mixed with the other components in the ratio SrM:MWCNT:aniline of 1 g:1–2 g:2 ml. The finished composites consisted of either agglomerations of MWCNTs coated in SrM/PANI, with some agglomerations of just SrM/PANI. The 10 nm MWCNTs were coated with an uneven layer of SrM/PANI, giving nanocomposites between 20 and 40 nm thick, with a MWCNT core (Fig. 55). The magnetic properties of these composites were very interesting, and are also shown in Fig. 55. The MWCNTs by themselves were soft magnets with a very low Ms of 0.4 A m² kg⁻¹, so small that above 0.3 T diamagnetism started to reduce the magnetisation, and with no measurable Hc. The SrM was a good quality material with a high coercivity, and PANI was as reported in Section 8.2. However, in the composite although Ms was greatly reduced, partly due to SrM volume dilution effects, Hc was actually increased to 593 kA m⁻¹, close to the maximum values reported for SrM. It was suggested that the PANI prevented the formation of large aggregates, and as a result the SrM became single domain at a dimension near the optimum for maximum coercivity. The conductivity increased from 2.5 to 6.6 to 7.2 S cm⁻¹, as the MWCNT content increased from zero to 1 g to 2 g, respectively, and the dielectric properties were poor as a result [492].
SrM coated oxidised-CNTs were also made using a citrate gel method, to give a nanocomposite containing 2 wt.% CNTs. With increasing reaction time at 80 °C (6–30 h), the SrM coating became increasingly dense, uniform and smooth, helped by the prior surface treatment of the CNTs, and ultrasonication to break the CNTs into shorter fibre lengths [493]. CNTs have also been used as a disposable template to make 25 nm spherical BaM NPs, by filling the CNTs with a BaM citrate precursor, which were then calcined at 1200 °C to obtain the ferrite NPs [494].

### 9.4. The potential of ferrite-fibre composites

It has been shown that properties such as thermal and electrical conductivity, and magnetic, electrical, optical behaviour can be enhanced in fibrous form [495]. The dielectric constant $\varepsilon^*$ of a fibre composite material depends not only on the $\varepsilon$ of the two composite components, but also on their geometry. The composite’s $\varepsilon^*$ can only be estimated, but if the geometry of the components is known the estimate approaches the true value, and this rule is also applicable to other properties, such as magnetic moment [496]. Dielectric properties are independent of the particle size or anisotropy of the fibre material, but for other properties which are so effected, such as magnetisation, this must also be accounted for.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_c$ / kA m$^{-1}$</th>
<th>$M_s$ / A m$^2$ kg$^{-1}$</th>
<th>$M_r$ / A m$^2$ kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrM</td>
<td>489.1</td>
<td>63.7</td>
<td>38.9</td>
</tr>
<tr>
<td>MWCNT</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>PANI</td>
<td>152.4</td>
<td>5.3</td>
<td>-</td>
</tr>
<tr>
<td>SrM / 2g MWCNT / PANI</td>
<td>593.4</td>
<td>8.9</td>
<td>5.3</td>
</tr>
</tbody>
</table>

**Fig. 55.** TEM image of SrM/2 g MWCNT/PANI nanocomposite, and the magnetic properties of the nanocomposite and its components [492]. The $y$-axes (M) of the magnetisation loops are not to scale with one-another.
If the fibres are continuous and unidirectional, purely independent material properties such as $\varepsilon$, thermal conductivity and density can be calculated from the rule of mixtures as purely additive. That is, the composite density, $\rho_c$, can be written as

$$\rho_c = V_m \rho_m + V_f \rho_f$$  \hspace{1cm} (9.1)

where $\rho_c$ is the composite density, $\rho_m$ and $\rho_f$ the matrix and fibre densities and $V_m$ and $V_f$ are the matrix and fibre volume fractions of the composite. A property such as thermal or electrical conductivity would approach the value of the most conductive material of the two, for example the metal in a metal-ceramic composite or the ceramic in a resin-ceramic composite [497].

Similarly, if a stress was applied parallel to the continuously aligned fibres the elastic modulus, $E$, will also behave in a purely additive fashion, unless the applied load is so large that the matrix deforms and a non-linear stress–strain curve develops [498]. In this case the less stiff composite component contributes little to the elastic modulus of the composite, $E_c$, so for a fibre reinforced composite

$$\rho_c \approx V_f E_f$$  \hspace{1cm} (9.2)

On the other hand, if the load is applied perpendicularly to the fibre alignment, each matrix component acts independently, so in this case

$$\frac{1}{E_c} = \frac{V_m}{E_m} + \frac{V_f}{E_f}$$  \hspace{1cm} (9.3)

Therefore continuously aligned unidirectional fibres produce anisotropic effects in directionally effected properties, with the strength and stiffness being highest parallel to the axis of alignment [497].

This has also been proved true for the magnetic permeability, $\mu$, of an aligned fibre, provided any demagnetising effects between individual fibres are ignored, as it can be for a composite with a volume fraction below the percolation threshold (less than 15–30%) [499]. The permeability, $\mu_{eff}$, of a fibre aligned parallel to an incident magnetic field can be calculated from

$$(\mu - 1)_{eff} = V_f (\mu - 1)$$  \hspace{1cm} (9.4)

Whereas for a fibre aligned perpendicular to the incident field,

$$(\mu - 1)_{eff} = \frac{V_f (\mu - 1)}{[1 + (\mu - 1)\gamma]/2}$$  \hspace{1cm} (9.5)

The change in the magnitude of the property at a varying angle between parallel and perpendicular to the axis of alignment is not a linear one, as can be seen in the varying strength of the layers in a 0°/30°/60°/90° pile E glass reinforced epoxy composite, where each successive layer of aligned fibre is rotated by an angle of 30°. The tensile strength in the 0° pile (parallel) is 7 times that of the 90° pile (perpendicular), but the 30° pile is only 2.5 times as strong and the 60° pile only 1.2 times stronger when the load is applied parallel to the 0° pile [497]. In the case of magnetic permeability, to get a good estimate of the total effective permeability contributions from all alignments of the fibre must be added. If a fibre is at an angle to the field it can be resolved into parallel and perpendicular components and the effective permeability will be the sum of these components. It is clear that in a fibre at an angle of 45° degrees to the incident field the contribution of the parallel component will be greater than that of the perpendicular component, so the effective permeability at 45° will have a value closer to that for the parallel fibre [499].

For fibres randomly oriented in a plane, where the plane = $xy$, it is a more complicated case but it has been shown [500] that $\varepsilon$ can be given, in the plane and perpendicular to it in the axis $z$, as:

$$\varepsilon_z = \varepsilon_m + \frac{2V_f (\varepsilon_z - \varepsilon_m)}{\varepsilon_z + \varepsilon_f}$$  \hspace{1cm} (9.6)

and

$$\varepsilon_x = \varepsilon_y = \varepsilon_m + \frac{V_f (\varepsilon_x - \varepsilon_m)(\varepsilon_x + 3\varepsilon_m)}{2(\varepsilon_x + \varepsilon_f)}$$  \hspace{1cm} (9.7)

Therefore, the attractions of producing composite materials with aligned hexaferrite fibre components are clear, for potentially directionally enhancing magnetic, and hence also MW, effects. This would also apply to MF or ME hexaferrite or composite fibres.
10. Hexagonal ferrite fibres

As shown in the previous section, it has been predicted that properties such as thermal and electrical conductivity, and magnetic, electrical and optical behaviour could be enhanced in material in fibrous form. This is because a continuous fine fibre can be considered as effectively one-dimensional, and it does not behave as a homogeneously distributed powder or sintered monolith. Although the intrinsic magnetisation of the material is unaffected, the effective magnetisation of an aligned fibre sample should be greater when a field is applied parallel with fibre alignment compared to when applied perpendicularly to fibre alignment [495]. The permeability and permittivity of pure cobalt metal fibres (at GHz frequencies, random alignment, 25 µm length) has been shown to depend upon diameter, their values increasing as fibre diameter was decreased from 3 to 1.5 µm [501]. Short iron fibres (2–5 µm diameter, 10–30 µm length), were shown to have microwave permeability and permittivity values between 14% and 127% greater when aligned parallel to the applied field than when parallel to it [502], and Nb₂O₅·TiO₂ single crystal fibres were found to have permittivity many times greater parallel to the fibre axis than perpendicular to it [503]. Single crystal SrM nanowires were grown by hydrothermal synthesis of NPs under a 0.35 T magnetic field, which resulted in nanowires 100 nm diameter and 2.5 µm long. The nanowires had Mₚ values of 59.3 A m² kg⁻¹, 36% higher than NPs made without the magnetic field, but an identical low Hₘ < 120 kA m⁻¹ [504]. The Taylor–Ulitovski method for the continuous fabrication of microwires coated by glass, known since the 1950s, forms glass-covered metal wires in a one-step melt spinning process, which have similar diameters to the ceramic polycrystalline fibres – an excellent review of the initial investigations into the magnetic properties of such wires has been published by Chiriac et al. [505]. Zhukov et al. have recently employed this method to produce long, thin ferromagnetic microwires, consisting of a tiny metallic nucleus (1–30 µm in diameter) coated by insulating glass-coating sheath (1–10 µm in thickness) [506]. The soft magnetic properties obtained in these Fe- and Co-rich microwires was explained as a consequence of the induced magnetic anisotropy, from the simultaneous action of large internal stresses and the axially applied magnetic field. A stress dependent giant magneto inductive effect has been found of 600% in Co₀.₇₀Fe₃.₈₅Ni₁.₄B₁₁.₅₅Si₁₄.₅Mo₁.₆₅ amorphous microwires, with nearly zero magnetostriction and optimal geometry [507].

However, there has been little research into the electromagnetic properties of fine ceramic fibres (<10 µm diameter), and the magnetic properties of hexagonal ferrite fibres were first investigated by the author. Pullar et al. reported a series of ferrites in the form of polycrystalline, continuous blow spun fibres produced rapidly and en-mass from a modified industrial process, not individually drawn metal wires or gel fibres pulled from a viscous gel. The difference between wires and fibres is not easy to define, but a good general definition of a wire is “a slender rod or filament of drawn metal”. whereas a fibre is “a specific form of chemically gelled fibrous materials manufactured into sheets, rods, tubes, and the like”. The fibres produced by Pullar et al. are in the form of a random “wool-like” mass, or as aligned fibre blankets or sheets, they cannot be separated or produced individually, and are characterised only as a bulk product. Consequently, magnetostrictive interaction between the fibres, misorientation of individual fibres, and shape anisotropy effects cannot be assessed for these materials, although work on magnetic microwires [508] has shown that significant differences may exist between the properties of individual fibres and blankets.

Pullar et al. reported the synthesis of a range of random and aligned hexagonal ferrite fibres, including BaM and SrM [71,72,77,156,304], Co₂Y [73,75,155], Co₂Z [75,155], Co₂W [74,75,155], Co₂X [76] and Co₂U [76] hexaferrites, as well as haematite (α-Fe₂O₃) and magnetite (Fe₃O₄ spinel) fibres [509], all blow spun from an aqueous inorganic sol–gel precursor. The fibres had diameters between 3–7 µm, and were collected as both continuous random fibres [357] and well aligned blankets (fibre length >30 cm). Images of some aligned fibre blankets are shown in Fig. 56, and they all had an alignment of >80% within ±20°, the best being Co₂Z with over 97.7% within ±20° and 75.6% within ±10° of the fibre axis [75].

In all cases the gel fibres were smooth and parallel-sided, with linear shrinkage >25% and a weight loss >45% when sintered up to 1250 °C. Although density was impossible to measure without destroying the fibres, their surface area reduced from >30 m² g⁻¹ to <1 m² g⁻¹ upon heating to 1000 °C, with a
corresponding loss of porosity, suggesting they were well sintered [155]. This was supported by the SEM images, which showed that M ferrite fibres consisted of densely-packed micron-scale grains (Fig. 57a), and the Co2Y fibres of randomly-oriented thin hexagonal plates (which often appeared to be needles when viewed end-on), up to 5 \( \mu \text{m} \) in diameter at 1000 \(^\circ\text{C}\) (Fig. 57b), which became thicker hexagonal plates up to 10 \( \mu \text{m} \) diameter and several microns thick at 1200 \(^\circ\text{C}\). The Co2Z ferrite fibres heated to 1000 \(^\circ\text{C}\) consisted of a mixture of micron-sized BaM and micron-range hexagonal plates of Co2Y (Fig. 57c), but with the formation of the Z phase at 1250 \(^\circ\text{C}\) DGG occurred. This led to the formation of greatly elongated hexagonal plates, which could be the width of the entire fibre and tens of microns in length, but only 1 or 2 microns thick (Fig. 57d). This compromised the strength of the individual fibres, but due to bonding between neighbouring fibres the resilience of the blankets on the macroscale was still surprisingly good. The Co2W and Co2U fibres exhibited a similar degree of DGG.

Fig. 56. SEM images of aligned hexaferrites fibres by the author, showing (a) BaM sintered at 1000 \(^\circ\text{C}\), (b and c) Co2Y sintered at 1000 \(^\circ\text{C}\), (d) 0.67% Ca-doped Co2Z sintered at 1200 \(^\circ\text{C}\), (e) Co2Z fibres sintered at 1250 \(^\circ\text{C}\), and (f) Co2W fibres sintered at 1200 \(^\circ\text{C}\) (SEM image mislabelled). In (e and f) DGG has induced a waviness in the individual fibres but not compromised alignment.
at 1200 °C and 1250 °C, but the Co₂X and 0.67 mol% CaO-doped Co₂Z had no such DGG at 1200 °C, and has maintained a much better fibre integrity.

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Fig. 57. SEM images by the author of the microstructure of hexaferrites fibres, showing (a) BaM sintered at 1000 °C (7000 × magnification), (b) Co₂Y sintered at 1000 °C (5000 × magnification), (c) Co₂Z sintered at 1000 °C, when it still consists of mixed M and Y phases (2000 × magnification), and (d) Co₂Z fibres sintered at 1250 °C, where DGG has occurred alongside formation of the pure Z phase (2000 × magnification). Size of grains indicated by the scale bar. Note that (c and d) are the same fibres at the same magnification, with just an increase in sintering temperature changing the microstructure.

Fig. 58. The alignment effects on magnetic properties of M ferrite aligned fibres [304].
The magnetic properties of random and aligned fibres were measured and compared, and as expected the random fibres had magnetic properties equivalent to that of powdered fibres or sintered powders made from the sol–gel precursors [357]. For the aligned fibres, those aligned parallel to the applied field had $M_s$ values slightly higher than those of the random fibres, whilst fibres aligned perpendicular to the field had $M_s$ values 62% and 75% lower, for BaM and SrM respectively [304]. There was no significant change in $H_c$ between random or aligned fibres of any orientation, and fibres aligned 45° and parallel to H had identical hysteresis loops (Fig. 58). This non-linear decrease in $M_s$ with increasing deviation from the fibre alignment is a feature seen in other alignment-dependent properties of fibres (see Section 9.3). This effect may also be enhanced by the imperfect alignment of the fibres, as although at least 80% were aligned within ±20° of the axis of alignment, many were not aligned directly along that axis, causing a spread of the alignment effect. There was virtually no change in $H_c$ or $M_r$ with alignment (Fig. 58). As $M_r$ varies greatly with orientation of domains, with the ratio $M_r/M_s$ being close to 1 along the c-axis in oriented BaM, but reduced to 0.5 in randomly oriented samples, the individual grains were clearly not oriented magnetically, and the alignment effects observed were purely due to fibre alignment, and not orientation of grains in the applied field. Therefore, properties along the axis of alignment were superior when compared to measurements perpendicular to the axis of alignment, giving a directionality to the magnetisation in an otherwise randomly oriented polycrystalline ferrite material (Fig. 58). The magnetic properties of other aligned hexaferrite fibres will be reported in the near future.

Composites were successfully made of these fibres based on both polymer resin and paper matrices. Many potential applications will involve the use of aligned fibres in a composite (aligned fibres will also have a greater volume fraction than random fibres in any composite materials), and they have potential applications in electronics, data storage, security and tagging (RFID), and EM wave absorbing materials/RAM.

BaM fibres with a diameter of 6 μm were made by an aqueous citrate gel method [510], with organic spinning aids added, and 350 nm diameter solid and hollow BaM fibres were made by electrospinning, and then sintered at 700 °C [511]. Although these later fibres were aligned, they showed a much smaller difference when $M_s$ was measured parallel and perpendicular to the fibre axis, and they had a low $M_s$ of ~50 A m² kg⁻¹ due to their nanocrystallinity. The fibres were made hollow through a two step heat treatment: in step 1, they were heated to 400 °C/30 min at a rate of 40 °C/min. This gave a dense outer shell, and upon subsequent heating to 700 °C, Ostwald ripening causes outward mass migration of the smaller inner crystallites to produce the hollow structure (Fig. 59). SrM nanofibres have also been made by electrospinning, using poly (vinyl pyrolidone) as a spinning aid, to produce random fibres. These were then sintered to produce SrM at 750 °C/2 h, with a grain size of ~40 nm forming a pearl necklace-like fibres between 40 and 100 nm diameter. These had $M_s$ = 57 A m² kg⁻¹ and $H_c$ = 385 kA m⁻¹, increasing to $M_s$ = 59 A m² kg⁻¹ and $H_c$ = 521 kA m⁻¹ with a grain size of 60 nm when sintered at 900 °C [512]. These were surprisingly high $H_c$ values for such small domains, and the peak $H_c$ at 60 nm suggested that below this critical single domain size the SrM is starting to approach the paramagnetic state. When these SrM nanofibres were substituted with La–Zn to make Sr₁₋ₓLaₓFe₁₂₋ₓZnₓO₁₉ ($x = 0–0.5$, calcined at 900 °C/2 h), as the grains size decreased with $x$ from 50
to 40 nm, so did $H_c$ from 413 to 219 kA m$^{-1}$ [513]. However, $M_s$ peaked at $x = 0.2$, with a value of 72 A m$^2$ kg$^{-1}$, considerably higher than the pure SrM nanofibres, but still with a much reduced $H_c \sim 325$ kA m$^{-1}$, due to the decrease in diameter to \sim 44 nm. The same authors have also reported Al$^{3+}$ substituted SrAl$_{1-x}$Fe$_{12-x}$O$_{19}$ nanofibres with an increased $H_c$ of 617 kA m$^{-1}$ and reduced $M_s$ of 25 A m$^2$ kg$^{-1}$ for $x = 2$ [514]. It can be expected that essentially one-dimensional hexaferrites, such as the micro- and nanofibres discussed above, will be of significant importance for the development of functional micro- and nanodevices in the future.

Song et al. have published a series of articles in 2010 detailing the preparation of M ferrite hollow fibres drawn from a citrate gel to produce fibres of 1–4 \mu m diameter, and up to 10 cm length, but not as aligned blankets. 1 \mu m BaM fibres sintered between 750 and 1050 °C had grain sizes between 38 and 72 nm, surface areas between 38 and 22 m$^2$ g$^{-1}$ and pores from 6.5 to 4.1 nm, respectively, and the fibres sintered at 750 °C had $M_s = 51.7$ A m$^2$ kg$^{-1}$ and $H_c = 232$ kA m$^{-1}$ [515]. They also made Ba$_x$Sr$_{1-x}$M hollow fibres sintered at 1000 °C, in which $M_s$ and $H_c$ decreased from 67 to 56 A m$^2$ kg$^{-1}$ and 440 to 320 kA m$^{-1}$ respectively, as $x$ went from zero to 1 (increasing Ba content) [516]. SrM hollow fibres were around 4 \mu m diameter, with the fibre walls being about 1 \mu m thick, and had a $M_s$ of 53.5 A m$^2$ kg$^{-1}$ and $H_c = 387$ kA m$^{-1}$ when sintered at 1100 °C/2 h. Again, these showed little variation in magnetic properties when measured parallel or perpendicular to the fibre axis, but the fibres were wavy and poorly aligned compared to those reported by Pullar et al. (Fig. 60) [517]. Song et al. made SrM/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composite fibres \sim 2 \mu m diameter drawn from a citrate sol–gel precursor, which had submicron ferrite grains of both phases, and a composite $H_c = 44.1$ kA m$^{-1}$, $M_r = 13.9$ A m$^2$ kg$^{-1}$ and $M_s = 66.5$ A m$^2$ kg$^{-1}$ ($M_r/M_s = 0.21$) when sintered at 1150 °C [518] (see Fig. 60).

They have also reported SrM/SrSiO$_3$ composite nanofibres made by electrospinning a viscous solution of nitrates and tetraethyl orthosilicate (TEOS), with SrSiO$_3$ content between 0 and 44 wt.% in the fibre fired at 800 °C/2 h [519]. XRD patterns showed poorly crystalline SrM with an amorphous background, which grew larger as the SrSiO$_3$ content grew larger, suggesting it was a non-crystalline phase. The nanofibres were <150 nm diameter, with 50 nm grains in the pure SrM fibres (Fig. 61a), and a

![Fig. 60. SrM hollow fibres by Song et al. [517].](www.iran-mavad.com)
decreasing grain size with increasing levels of SrSiO$_3$ (Fig. 61b) down to 7 nm for 44% SrSiO$_3$, observed by HRTEM (Fig. 61c and d). The fibres with >32% SrSiO$_3$ appear smooth and dense, with improved mechanical properties. The magnetic measurements of the fibres are shown in Fig. 61e-g, and it is clear that $H_c$ decreases greatly with decreasing grain size (increasing SrSiO$_3$ content). The fibres are a hard magnetic materials between 13% and 32% SrSiO$_3$ ($H_c = 359 \rightarrow 200$ kA m$^{-1}$ at RT) as grain size

Fig. 61. SEM images of (a) pure SrM nanofibres and (b) 38 wt% SrSiO$_3$/62 wt% SrM nanofibres. TEM (c) and HRTEM (d) images of SrM nanofibres with 44% SrSiO$_3$. (e) RT magnetic hysteresis loops of SrSiO$_3$/SrM nanofibres (% SrSiO$_3$ indicated). Plots of variation in $H_c$ with (f) grain size and (g) SrSiO$_3$ content at RT and 77 K for SrSiO$_3$/SrM nanofibres. All fibres fired to 800 °C/2 h [519].
decreases from 25 → 17 nm. Then, with 38 % SrSiO₃ (14 nm) \( H_c \) reduces massively to a soft 16 kA m⁻¹, and with levels of 41% and 44% SrSiO₃ the fibres become fully superparamagnetic, with a greatly reduced \( M_r \) from 28 to 9 A m² kg⁻¹, all at RT. This transition from ferrimagnetic to superparamagnetic between 32% and 38% SrSiO₃, representing a reduction in grain size from 17 to 14 nm, is even more apparent in the measurements taken at 77 K. This shows that the critical domain size at which SrM becomes superparamagnetic is <15 nm in these fibres, and the fibres with 44% SrSiO₃ had a grain size of 7 nm, \( M_s = 7 \text{ A m}^2 \text{ kg}^{-1} \) and \( H_c = 5 \text{ kA m}^{-1} \). It should be noted that the amorphous SrSiO₃ phase did not greatly reduce magnetisation more than would be expected as a compositional effect (\( M_s = 54, 38 \) and 31 A m² kg⁻¹ with 13%, 24% and 32% respectively, at RT), but allowed a control over grain size, and that these effects are largely due to the domain size of the SrM. Nevertheless, the chemical composition of the composite will also affect these results, which is why the critical domain size is so low here. The same team recently reported dielectric/magnetic composite 1:1 SrTiO₃/SrM nanofibres, also electrospun, with diameters of 120 nm. These had excellent magnetic properties when calcined at 950 °C [520]. Another group has made electrospun thermoplastic ester elastomer fibres were coated with a SrM citrate-gel precursor and calcined at 800 °C to produce SrM microtubes and 200 nm diameter nanorods, although these had low aspect rations after processing and no longer resembled fibres. A Fe:Sr ratio of 11 was required to produce a single phase M ferrite without α-Fe₂O₃ as well, and the product has low \( H_c \) values between 150 and 205 kA m⁻¹ [521].

11. Nanoscale hexagonal ferrite particles, ceramics and powders

For the purposes of this section we will consider nanoparticles (NPs)/nanocrystals (NCs)/nanoscale artefacts to be below 100 nm in dimension, and disregard thin films, as this subject would be deserving of a review all of its own. When at the sub-100 nm scale, the NPs are below the critical minimum domain size for maximum coercivity, and \( H_c \) will decrease greatly with decreasing grain size as the domain size at which the hexaferrites become superparamagnetic is being approached. Normally, any ferromagnetic or ferrimagnetic material undergoes a transition to a paramagnetic state above \( T_c \). Superparamagnetism is the random flipping of magnetisation in single domain particles, which can happen if the thermal energy is greater than the anisotropy energy, and happens above a temperature known as the blocking temperature (Stoner–Wohlfarth Theory). As this temperature increases with volume, in a particle that is small enough it can come down to useful temperatures, e.g. below 273 K so a material is superparamagnetic at room temperature. In this superparamagnetic state, magnetisation can randomly flip direction so that it appears to average zero in the absence of an applied magnetic field. An external magnetic field is able to magnetise the nanoparticles, which still have a large magnetic susceptibility so they can show a significant magnetisation, but they will have no hysteresis and magnetisation will pass through zero (i.e., \( H_c = 0, M_r = 0 \)). \( M_r \) is also usually considerably smaller than for the ferrimagnetic form, as surface effects dominate in such a small particle, and thermal fluctuations of magnetic moments cause surface spin canting and non-collinear spin effects. Therefore, as the particle size decreases below the critical domain size for maximum \( H_m \), the blocking temperature decreases, and as the critical size for superparamagnetism at a given temperature nears, \( M_r \) decreases and \( H_c \) approaches zero. Eventually \( H_c \) will equal zero and there is no hysteresis, and therefore negligible \( M_r \), as a truly superparamagnetic state is reached. This should happen at a domain size of around 10–20 nm for BaM.

One obvious limitation of this is that superparamagnetic NPs cannot be used in applications that require \( M_r \), such as data storage, and this puts a minimum size limit on hexaferrites for such applications. However, superparamagnetic hexaferrites are still of great interest for other potential applications, where a switch between a magnetic “on” and “off” state would be required. Magnetic NPs above the critical grain size for superparamagnetism could be used for high density information storage. Nanoscale self assembly during synthesis or processing opens up intriguing new avenues for exploration. Biomedical applications of magnetic NPs are constantly increasing, such as MRI contrast agents, hyperthermia (heating targeted tissues with NPs under an applied magnetic field to between 41 and 46 °C to kill cancer cells), target drug delivery and cellular imaging. Several clinical trials have already been undertaken using magnetic NPs to detect liver and lymph node tumours, as well as inflammatory and degenerative diseases [522]. The NPs investigated so far for biomedical uses have been α- and
γ-Fe₂O₃, Fe₂O₃·CoO and spinel ferrites. MgFe₂O₄ NPs with \( M_s = 15.3 \text{ A m}^2 \text{ kg}^{-1} \) and \( H_c = 5 \text{ kA m}^{-1} \), and diameters between 20 and 50 nm, have proved to be ideal for magnetic hyperthermia applications [522]. Obviously the high frequency properties and resonance losses of hexafermites (generating localised heat) make hexafermite NPs interesting candidates for biomedical applications, although the problem of barium or strontium retention within the human body is an issue for in vivo treatments.

For BaM, the critical domain size below which \( H_c \) rapidly decreases as the superparamagnetic state is approached is usually taken to be around 60 nm [523], although this can vary greatly with chemical composition, morphology, strain and defects. In the SrM–SrSiO₃ composite fibres discussed in Section 9 is was as low as 15 nm [519], and in SrM made at 15 and 40 nm \( M_s \) increased from 2.4 to 75 A m² kg⁻¹, suggesting the critical domain size is between these two values [524]. The BaM NPs with diameters of 50–100 nm, made by the enhanced microwave auto-combustion process in Section 3.9, had \( M_s = 64.1 \text{ A m}^2 \text{ kg}^{-1} \) and a low \( H_c \) of 20 kA m⁻¹ [100]. The critical domain size is reported as being around 90 nm for Co₂Z NPs made from a stearic acid sol–gel, which appeared to be single phase Co₂Z at only 950 °C with \( M_s = 44 \text{ A m}^2 \text{ kg}^{-1} \) and a peak \( H_c \) of nearly 30 kA m⁻¹ for the 90 nm diameter particles [525]. This decreased to 15 kA m⁻¹ when the size was only 60 nm at 850 °C, and the NPs still appeared to be Z ferrite from their XRD pattern. Stearic acid sol–gel synthesised Co₂X NPs with a very small size of ~20 nm had a very low \( H_c \) of 10 kA m⁻¹, which rose to a maximum of 27.5 kA m⁻¹ at a size of 45 nm, after which it decreased linearly [82]. This suggests the critical domain size is around 50 nm for Co₂X. Co₂U NPs were also made by the stearic acid sol–gel process, and with a size of 50 nm \( H_c \) was a minimum of ~20 kA m⁻¹ [83]. These results suggested that Co₂U becomes superparamagnetic below the critical domain size of 80 nm [390]. However, these X and U NPs had a highly non-stoichiometric surface, which will effect the magnetic properties of such small particles, and \( M_s \) increased linearly with grain size, suggesting the surface effects were important. The stearic acid sol–gel methods does appear to be a simple process for making relatively monodisperse hexafermites NPs, and the sizes of the Co₂X and Co₂U NPs were confirmed by three methods: TEM, XRD line broadening (suggesting there were single NCs) and surface area measurements. Nanocrystalline single phase SrM powder of around 10 nm diameter was obtained at only 250 °C from a sol–gel precursor when fired in an oxygen atmosphere [179], and SrM NPs made from a microemulsion process (Fe:Sr = 11) and calcined at 700 °C were 50–100 nm in diameter, with \( M_s = 55 \text{ A m}^2 \text{ kg}^{-1} \) and \( H_c = 39 \text{ kA m}^{-1} \), although they still contained traces of \( \alpha \)-Fe₂O₃ [526]. In a sol–gel technique with stearic acid as the chelating agent, single phase BaM crystallised from the precursor at 700 °C, and 20 nm NCs were formed using stearic acid which were superparamagnetic [154]. It should be noted that many articles report nanoscale ferrites based purely on the crystallite size derived from the Scherrer equation of XRD line broadening. This does not necessarily relate to the grain size, and only papers with SEM/TEM or superparamagnetic evidence of NPs are considered here.

Hydrothermal synthesis is gaining interest as a relatively controllable way of making true hexafermite NPs. The hydrothermal synthesis of an extremely barium-rich mixture of FeCl₃:Ba(OH)₂:BaCl₂ in the ratio of 1:3:3 were reacted at 140–200 °C/12 h resulted in some BaM NPs, which were separated from Fe₂O₃ and hydroxide/hydrate compounds by washing with HCl. The average diameter (measured by TEM) of the NPs increased from 9 to 15 nm as reaction temperature increased, and XRD showed them to be single NCs [527]. The yield was also claimed to increase with temperature, although no details of this are given and it is suspected that all yields were low, and after a critical reaction period (>12 h) a significant grain growth occurred. The product consisted of the small platy NPs and larger nanorods, 50 nm long, the proportion of which increased with synthesis temperature. However, these two phases could be separated by centrifuging, and details are given of this process. The separated, as-synthesised NPs had \( M_s = 10 \text{ A m}^2 \text{ kg}^{-1} \) and \( H_c = 18.3 \text{ kA m}^{-1} \) when 9 nm, and \( M_s = 15 \text{ A m}^2 \text{ kg}^{-1} \) and \( H_c = 47.0 \text{ kA m}^{-1} \) when 15 nm. The volume of these NPs was ~1 nm³, a similar dimension to the unit cell volume of BaM, so surface demagnetisation effects dominated and greatly reduced \( M_s \), but \( H_c \) was still surprisingly large for such small NPs.

Several articles referred to earlier in this review mention the synthesis of nanopowders, or NPs but with a wide range of sizes (large polydispersity). However, the really exciting developments in nanoscale synthesis involve the wet synthesis of hexafermite NPs or NCs using capping agents to limit the reaction, and therefore the size, of the NPs. If such NPs are very monodisperse (little variation in size), they will tend to self assemble as well. Barium and iron nitrates coprecipitated at room temperature,
with polyacrylic acid (PAA) as a capping agent to limit particle size (ratio of Fe:Ba = 11), resulted in highly monodispersed NPs with an average diameter of only 4.5 nm with a standard deviation of 0.8 nm. Pure BaM crystallised from the amorphous nanoparticles at 700 °C, to form BaM nanocrystals between 23 and 34 nm in diameter that agglomerated after the burning off of the PAA. After heating to 800 °C the crystallinity improved, and the size range increased to 49–82 nm. SQUID measurements gave \( M_s = 36.9 \) and 60.8 A m\(^2\) kg\(^{-1}\) and \( H_c = 9.3 \) and 17.7 kA m\(^{-1}\) for the nanoparticles heated to 700 and 800 °C, respectively, demonstrating that despite their high \( M_s \) value the nanocrystals were still approaching superparamagnetic with a very low coercivity even up to 80 nm diameter [528]. The form of the iron oxide precursor has also been reported as having a great effect on the size of the resultant ferrite powder – when made from a mixture of BaCO\(_3\) and goethite (\( \alpha \)-FeO(OH)) powders heated to 675 °C/1 h, 100 nm NPs of pure phase BaM resulted, with good ferrimagnetic properties (\( M_s = 60 \) A m\(^2\) kg\(^{-1}\), \( H_c = 358 \) kA m\(^{-1}\), \( M_r = 0.5 \)) [529].

To prepare uniform, monodisperse NPs, the nucleation and growth stages must be separated. Therefore, after initial nucleation, a state must be reached where no new nucleation occurs, but a

![Fig. 62. TEM images of (a) 50 × 3 nm BaM platelets synthesised at 280 °C/5 h [89], and well monodisperse BaM NP discs <10 × 3 nm diameter synthesised at (b) 80 °C/24 h viewed from the top, and (c) 120 °C/24 h viewed edge-on showing the (002) BaM planes, made by hydrothermal nanosynthesis [530]. (d) RT magnetisation curves of Ba NPs synthesised at 80–140 °C/24 h [530].](image)
process of continuous dissolution and reprecipitation on existing crystallites limiting the growth of the crystallites. This final size can be controlled by the amounts of precursors, reaction conditions, and concentration of the solution. Drofenik et al. have made well monodisperse BaM NPs with diameters below 10 nm via hydrothermal synthesis, the first truly superparamagnetic BaM NPs reported. They initially produced reasonably monodisperse hexagonal platelets 50 nm wide and 5 nm thick (Fig. 62), from a $\gamma$-Fe$_2$O$_3$-Ba(OH)$_2$ precursor with Fe:Ba ratio of 4 and a low concentration of <1 wt% in a sodium hydroxide solution [89]. This was heated in a sealed autoclave in a hydrothermal reaction at 280 °C/5 h to form pure BaM NPs, which had a lowered $M_s$ of 40 A m$^{-2}$ kg$^{-1}$, and an even smaller $H_c$ of 96 kA m$^{-1}$ than expected for their domain size, due to poor crystallinity. However, BaFe$_4$O$_7$ tended to form if Fe:Ba <4, and $\alpha$-Fe$_2$O$_3$ if >4, and they also found that when the solution was diluted to less than 1/4 of the original concentration, BaFe$_4$O$_7$ formed as well. Having noticed that concentration of the precursor solution had a great effect on particle size in hydrothermal synthesis, and that a large excess of hydroxyl ions (OH$^-$ : NO$_3^-$ = 30) drastically reduced the synthesis temperature, they then discovered that the addition of a surfactant such as oleic acid (commonly used as a capping agent in nanosynthesis) could arrest secondary recrystallisation and particle growth of the resultant NPs [90]. Drofenik et al. have now optimised this process to such an extent that they can produce well monodisperse NP discs <10 nm wide and 3 nm thick (Fig. 62) in an autoclave at extremely low temperatures between 80 and 120 °C/24 h, with a sample concentration of 0.4 mol L$^{-1}$ Fe$^{3+}$, in a highly concentrated sodium hydroxide solution with a Fe:Ba ratio of 5, and no capping agents required [530]. The highly basic solution encouraged the formation of the tetrahydroxoferate (III) complex ion, [$\text{Fe(OH}_3$]$^{3-}$, which tends to associate in iron-rich aggregates, and thus formed BaM in the correct conditions, despite the highly non-stoichiometric mix. They also found that an increase in precursor concentration had no effect on particle size, and suggested that the release of large amounts of OH$^-$ in the BaM formation process encouraged nucleation and growth of new BaM NPs, thus preventing Ostwald ripening and grain growth. The NPs made at 120 °C were shown with TEM to be discs 7 nm wide and only 3 nm thick (Fig. 62), not much higher than the Ba unit cell (2.318 nm), with the c-axis oriented perpendicular to the plane of the disc. TEM and EDS confirmed their composition to be pure BaM, although XRD patterns had very broad or missing peaks due to their small grain size. The NPs made at 80 and 100 °C where superparamagnetic, with no measureable $H_c$, and as synthesis temperature increased to 120 °C the NPs began to have magnetic hysteresis and $M_s$ increased from ~2 to 10 A m$^{-2}$ kg$^{-1}$, still a very low value due to the domination of surface magnetism effects (Fig. 62) [530].

Such monodisperse NPs can be easily coated in silica shells by the Stöber process (using hydrolysed tetraethyl-orthosilicate, or TEOS), to create hybrid ferrite@SiO$_2$ core–shell NPs. This silica shell is
hydrophilic, biocompatible, and can be easily functionalised with a wide range of organic, metallo-organic, luminescent, biological and bioactive compounds, for applications in biomedicine and sensing. The thickness of the shell can be determined by the conditions of the Stöber process (Fig. 63). BaM nanorods were made by adding polymethylmethacrylate to a citrate gel of BaM, drying it and firing it directly to 850 °C/1 h without a prior combustion stage. The as-synthesised material was claimed to consist of nanorods 60 × 300 nm, although from the published SEM images it does seem that at least some of these are hexagonal plates viewed sideways on. The authors explain a mechanism whereby PMMA microspheres coated with a layer of precursor gel slowly decompose to gas over 230–430 °C, collapsing to an oval and then tubular shape under gravity as the volume decreases. Certainly the PMMA template does effect the morphology of the grains, as does changing the ratio of PMMA to BaM [531].

It should be mentioned that present knowledge concerning the ecotoxic effects of nanomaterials is very limited and needs to be investigated more fully. There are many fears in the general public about nanomaterials, some justified and some not, and it becomes particularly relevant if hexaferrite NPs are to have wide spread use, or be used in in vivo biomedical applications. Many materials are particularly harmful to aquatic species. The toxicity of various metal oxides, ferrites (including SrM) and CNTs, was examined and bioassayed across several taxonomic aquatic groups including decomposers (bacteria), primary producers (micro-algae), as well as primary and secondary consumers (micro-invertebrates and fish) [532]. Of all the materials investigated, SrM was the least harmful along with C_{60}, and less harmful than either CNTs or TiO_{2} NPs, for example. YIG, and Ni/Zn and Cu/Zn spinel ferrites were all more toxic than SrM, especially to invertebrates. Most of the materials tested were toxic, but SrM was only harmful (the lowest rating) at high levels of 10–100 mg/L to two groups tested (MARA bacteria and H. Attenuata invertebrate secondary consumers), and was non-toxic to all the others, including fish. This indicates that hexagonal ferrites which do not contain problematic TM ions will be relatively non-harmful NPs in real-world applications.

12. Applications of hexagonal ferrites

Magnets are used in a multitude of applications, for example motors, generators, transformers, actuators and sensors, information storage, mobile communications, transport, security, defence and aerospace, diagnostic devices and to focus electron beams. The most used magnetic materials are ferromagnetic metals and alloys or ferrimagnetic ceramics. Of the ceramics, by far the most used are hexagonal ferrites, and some of their multitude of applications are shown in Fig. 64. The total number of patents and papers on hexagonal ferrites are shown by country in Fig. 65, and it can be seen that

![Fig. 64. Many of the practical applications of hexaferrites [485].](www.iran-mavad.com)
the US dominates the patents market. Some Asian countries such as China and Japan have been seri-
ously involved in hexaferrites research for decades, as was the Soviet Union. However, the newer rap-
idly emerging economies such as China, India and Brazil are becoming increasingly important players
(and in the case of China the major contributor) of research into hexagonal ferrites, driven largely by
mobile communications and defence needs, and are challenging the traditionally more technological
Western countries and Japan and Korea.

12.1. Permanent magnets

The best permanent magnets are made from alloys of rare earth metals, especially neodymium, but
due to increasing scarcity, and more or less a single source of production (97% of rare earth metals
come from China, and they have started to sell the higher cost manufactured magnets rather than
the raw materials), the cost of rare earth magnets has increased by up to 500% recently, and will con-
tinue to rise [533]. Permanent magnets made from hard ferrites are not as good as alloys, but they are
far cheaper and easier to make, and hexagonal ferrites are used in all of the applications mentioned
Permanent ferrite magnets are usually made as either sintered magnets (a pressed ceramic powder) or bonded magnets (made as a composite by extrusion or moulding) – see Fig. 66. Bonded dust magnets, made of BaM in an elastic or plastic binder to make a plastoferrite (see Section 12.4) which is easily workable and can be cut into any shape, are familiar to all of us as fridge magnets, both on and inside the door. Magnetic materials for good permanent magnets need to be hard magnetically, and resistant to demagnetisation. Therefore, they need to have stable domains, and must have a large remanence and coercivity. A large, square loop with a high energy product is also preferable, so more energy is needed to demagnetise the material. The M ferrites are ideally suited to such applications.

In the 1970s hard ferrites took the lead over alloys in world production, with 80,000 tonnes manufactured in 1977 [143]. Common uses of ceramic M ferrite magnets are in loudspeakers, windscreen wiper motors and other small electric motors, relays, clocks, magnetic separators, correction magnets in cathode ray tubes, magnetrons, used to direct electrons into a spiral path and generate microwaves, dynamos and holding magnets. In 1974, 65% of permanent magnets were used in the communications industry (and 70% of those as loudspeaker magnets), 20% for brake coupling and sealing devices and 15% in dynamos and motors. Today the most common uses for hard hexaferrites are still as permanent magnets in refrigerator seal gaskets, microphones and loud speakers, small motors for cordless appliances and in automobile applications (a modern car may contain over 100 small hexaferrite-based motors and sensors). For this reason, M hexaferrites account for over 90% of the total permanent magnetic materials manufactured globally [534], with 50 g of BaM alone produced for every man, woman and child on the planet each year [1]. Soft hexaplana ferrites are also very important as cores for RF transformers and power supplies, especially at higher frequencies, and new materials with much lower power losses are now required to save energy. In 1999 the M ferrite world market was worth $4.8 billion (57% of the permanent magnet market) [535], and they were still the most economically important permanent magnets in 2007 (Fig. 67). Even though they are much less expensive that neodymium magnets, especially with the large recent increases in cost and production of Nd magnets, ferrites are still extremely valuable permanent magnets because of the huge volumes produced (Fig. 68), accounting for 34% of the global sales of $11 billion in 2010 [536].

Global sales of all permanent magnets have been predicted to rise to over $20 billion by 2020, with over one million tonnes of ferrite produced annually. Two increasingly important markets globally for permanent magnets are in motors for electric-powered cars, and generators in wind turbines. As the scarcity and cost of neodymium magnets increases, hard ferrites will become economically more attractive as magnets for these applications, despite their inferior properties, especially for smaller wind turbines.

12.2. Electrical and microwave devices

In our modern world there is constantly an increasing demand for signal processing devices in mobile communications, radar detection and instrumentation, satellites and GPS, wireless communications and fee collection, security and defence, aerospace, and automotive and anti-collision...
applications. Furthermore, the operating frequencies are always moving progressively higher, from MW to millimetre wave, requiring the use of hexagonal ferrites. The US, international and military standard frequency bands and the uses of the MW spectrum are shown in Fig. 69, and those of particular interest for applications of hexagonal ferrites are between 1 and 110 GHz. Various regions within each band are reserved for radar (civilian aeronautical, marine and meteorological), mobile, wireless and fixed telecoms, satellites, GPS and radiolocation, broadcasting, space research and astronomy. Military use also covers these bands, and military interest includes imaging through solid objects and EM disabling systems.

Depending on the applications, either hard or soft ferrites can be required. However, for use at MW frequencies the MW dielectric losses must be minimised, which often requires the ferrite to be a good electrical insulator and have a moderate permittivity to allow a full penetration of the electrical field. As we have seen this can be a problem with the hexaferrites, and one solution has been to fabricate ferrite components on a superconducting substrate to eliminate conductor losses [538], or as a composite in a non-conductive matrix. Some of the most important hexaferrite MW applications are as non-reciprocal devices such as antennas, circulators (that only allow the circulation of the signal in one direction around a circuit, also known as duplexers) and isolators (that allow the signal to go forwards, but absorb it if it reflects back), which enable the use of one component to transmit and receive. They effectively switch between transmitting and receiving. Magnetostatic MW devices such as delay lines, filters (multilayer inductors), resonators, and non-linear devices (e.g., power limiters) can be tuned over a broad operating frequency range by external fields. More details on microwave ferrites and their applications can be found in the review by Ozgur et al. [1]. EM absorbers and RAM are discussed in Section 12.5.

Often the ferrite is expected to do work, enhancing the magnetic field as an electrical current is passed through it. Such devices include the cores of electromagnets, motors, transformers, and generators, using AC currents. As the magnet must be cycled through the hysteresis loop continually and rapidly, so the energy product of the loop should be as low as possible. Hence a small coercivity
and remanence is desirable, but the material must also have a high magnetic saturation and permeability to generate a sufficient induced magnetisation. Therefore, the ferroxplana ferrites are ideally suited for such applications, as despite being soft magnets from the rotation of the anisotropy within the plane or cone of magnetisation, they also have high magnetic permeabilities. Self biasing devices have a variable permeability which can be tuned by applying an external field, usually from a solenoid, which adjusts the anisotropy field. Such devices require ferrites which have high $M_s$, high $M_r$ so they retain the bias when the field is removed, but a low $H_c$ so a small field is required to vary the bias. Much more detail can be found on the theory and characteristics of passive MW ferrite devices in the second part of the review by Ozgur et al. [539].

The material must also have a high electrical resistivity and a rapid realignment of domains in response to high frequency magnetic fields to minimise the energy losses. If the frequency of the applied field is too high the domains cannot realign each cycle causing the device to overheat due to dipole friction. At higher frequencies there is also more heating due to the completion of more cycles per second, resulting in the loss of more energy. Most hexagonal ferrites have a high resistance and therefore very low eddy current losses, so they are well suited for high frequency applications, at radio and microwave frequencies, especially if the remanence is raised. The total loss in MW devices is mainly determined by magnetic damping from FMR, so development of hexaferrites with narrow FMR line-widths to limit these losses is a major goal. As is stands, most MW applications (apart from absorption) use off-resonance frequencies away from FMR to minimise losses, where the off-resonance or effective line-width is more relevant.

Although BaM has been widely used for various microwave device applications for several decades, the next-generation of such devices cannot be smaller, weigh less, and be more efficient. A recent trend in microwave technology is the integration of ferrite passive devices (e.g., circulators, isolators, phase shifters, filters, etc.) with semiconductor active devices (e.g., amplifiers, switches, and signal processing devices) onto a single planar system platform such as a Si wafer. This meets the demands of increasing systems integration, while also reducing device profile, volume, and weight. This necessitates the growth of high crystal quality ferrite films on semiconductor substrates. It has been demonstrated that high crystal quality is responsible for low microwave losses in ferrite films. Because of chemical reactivity, interfacial diffusion, poor lattice matching, and complications related to the high temperatures needed for the deposition of ferrites, the growth and processing of highly-oriented BaM films on semiconductor substrates remains a significant challenge. These process temperatures, typically ~900 °C, lead to the degradation of most semiconductor materials. LTCC or NP hexaferrites need to be developed as an alternative to deposited thin films.

12.3. Data storage and recording

In digital memories a bit is stored as either 0 or 1, so a square loop with a big remanence is required to ensure the data remains stored and is not lost accidentally, and a high signal to noise ratio is
required to reduce error rates. However, in re-recordable memories low saturation magnetisation and coercivity are required so small fields can be used to overwrite the data. In both cases chemical stability and longevity of the magnetisation is vital [540]. Traditional commercial products included audio tape, VCR tape, Professional Hi-8 mm data tape, Sony DAT tape, floppy discs, and rigid or hard discs.

BaM and SrM are used for high density magnetic recording and magneto-optical recording, being chemically stable and mechanically strong, and with high saturation magnetisations. Oriented ferrites are used in both longitudinal and perpendicular recording, in which the magnetic anisotropy of the material is aligned respectively parallel or perpendicular to the recording media. In longitudinal recording the magnetic media is usually an acicular particulate of single domain size, with the longer axis aligned parallel with the direction of motion past the recording head, whereas perpendicular media consist of a polycrystalline thin film with the grains aligned parallel to the direction of motion.
of the disc, and not the head. However, BaM or SrM films deposited without any substitution have met several problems for high-density magnetic recording: they have a large positive temperature coefficient of coercivity, the grain size in such films is in the order of $10^2$ nm, and with a decrease in grain size the magnetisation becomes thermally unstable, requiring a larger magnetocrystalline anisotropy. The coercivity of M ferrites is also too high for many recording applications, because a large magnetic field would be required to record and re-record data, but it was found that in doped M ferrites all these properties could be tailored with varying substitution [541].

Cobalt–titanium doped M ferrites were first developed for recording by Toshiba in 1982, and they are particularly suited for use in recording media such as magnetic tape when coated as a thin film onto a substrate, as the grain size and coercivity can be lowered considerably but without much loss of magnetisation in the ferrite [333]. It is important that such materials have low switching fields, low magnetic losses and high signal-to-noise ratios, and all of these criteria are satisfied by the range of CoTiM ferrites. The ideal substitution level for longitudinal recording in BaCo$_x$Ti$_x$Fe$_{12-x}$O$_{19}$ was found to be $x = 0.7$, with a coercivity of $88$ kA m$^{-1}$ [340], which is around the lower limit for this kind of application [542]. Additions of Cr$_2$O$_3$, ZrO$_2$, or Y$_2$O$_3$ [543], and La–Zn substituted M ferrites [544] were used to reduce grain sizes down to a few tens of nm, suitable for high density recording media.

Currently, large capacity data storage media are required due to the huge increases in worldwide data storage volume. Ideal modern high density recording devices need an information density of >2 GB cm$^{-2}$ (>13 GB per square inch) and a high coercivity, but the grains should be as small as possible to increase signal-to-noise ratio and bit density, and magnetically isolated from each other to minimise transition noise [542]. In 2006, in collaboration between Fujifilm and IBM, a world record in data density on linear magnetic tape was achieved using BaM particles with a density of 6.67 GB per square inch. In 2010 they demonstrated a new world record in area density on linear magnetic tape, with an area density of 29.5 GB per square inch with magnetic tape media using BaM nanoparticles (particle volume of 1600 nm$^3$). This is 1/3 of the current smallest usable metal particle volume, and offers higher coercivity, lower noise, higher frequency characteristics and superior storage performance than metal particles. They claim this points to the possibility of developing a single tape cartridge capable of holding 35 terabytes, nearly 44 times the current data capacity of today’s industry most popular standard magnetic tape products [545]. At the beginning of 2011 Fujifilm announced the commercial production of a data cartridge is manufactured using these BaM particles, with a native storage capacity of 5 TB and transfer speed of 240 MB s$^{-1}$, a capacity increase of five times their current 1 TB StorageTrek drive [546]. One of these new data tapes could store the equivalent of 8 million books. Even today the data storage tape market is still very large, as tape data libraries consumes little space and energy compared to hard drives, and according to IBM the market was worth $4.8 billion in 2005, and they predict a growth of up to 8% in 2011.

BaM thin film recording media cannot have a protective coat for wear or erosion resistance, as these devices need a very low flying height for the recording head. Particulate media magnets are better than thin films in so far that they can have a better wear resistance, but they also tend to have lower magnetisations. One way around this is to make a composite ferrite consisting of two phases, such as BaM coated with nanocrystalline $\gamma$-Fe$_2$O$_3$ or CoFe$_2$O$_4$. The magnetic bubble memory is a recording device which was first studied in BaM single crystals [547]. If a polycrystalline sample of BaM was arranged so the c-axis is perpendicular to the hexagonal plane, and it had a small enough particle size, each grain carried a single bit of information in a cylindrical “bubble” domain. This kind of memory still has potential for use in computing, if a small enough grain size can be achieved to maximise the information density.

Recent advances in MF hexaferrites which have ferroelectric-like behaviour at room temperature, and in which polarisation can be switched by small magnetic fields, could potentially lead to novel magnetically-rewritable ferroelectric memories and an electrically rewritable magnetic memories in the future.

12.4. Plastoferrites

Plastoferrites, or bonded magnets, are magnetic composite materials in which a powder of a ceramic ferrite is incorporated into a resin or thermoplastic matrix. These have diluted magnetic qualities
due to their composite nature, but the products are not brittle and fragile, and are hard to break or crack. They can be cut, stamped and shaped, in a highly mass productive and therefore cheap process, and complex shapes are possible with a high degree of dimensional precision. These include flexible sheets (Fig. 70), very long or thin shapes and radially oriented materials, and many electrical components are manufactured in this way [143]. In the preparation of resin encapsulated ferrites compressive stress can be induced as the resin sets, and if the material has a negative magnetostriction \( M_r \) will increase at the expense of \( H_c \). Therefore, resins which shrink a lot or harden unevenly should be avoided, and some resins also generate extreme localised heat as they set, which could affect the magnetic properties [114]. Plastoferrites are most familiar as refrigerator door magnets, both the decorative type on the outside and the magnetic sealing strips inside the rim of the door.

12.5. RAM and microwave/EM wave absorption

The constantly increasing use of devices operating at MW frequencies in our immediate environment, such as radar and wireless and mobile communications, has resulted in a great increase in EM interference, as well as in the intensity of this ever-more-present non-ionising radiation. The has lead to a growing requirement for MW absorbing materials to reduce interference, shield equipment, shield rooms and chambers for EM compatibility (EMC) testing, and to minimise the harmful effects of EM waves on biological tissues. Ferrites are used as microwave absorbers – they can absorb the MW energy around the frequency at which FMR occurs. They are already used as EM absorbers to shield rooms and chambers used for EMC testing of new products and devices at MW frequencies. Absorbers can be produced as ceramics or as composites, typically plastoferrite tiles for EMC applications. The EM properties of composites can be effectively tuned simply by varying the volume fractions of the constituent phases. In addition, a synergistic effect between the properties of the constituent phases may also be observed in some composites. For this reason, magnetic composites are interesting for microwave applications, and the properties of some composites are discussed in Section 8.

Modern military radar tend to use the X and K bands (8–40 GHz), often pulsing over a range of frequencies), the shorter wavelengths allowing higher resolution. Radar absorbing paints or coatings made from ferrites can be used to coat military aircraft for stealth operation, and have also been applied to ships and both naval and ground-based platforms. They absorb some of the radar signal beamed at the target, reducing or disguising the radar cross section signature that is then detected at the other end – it does not make the target totally radar “invisible”. This is known as “stealth” or “low observable” technology. There is a huge interest in hexaferrites as RAMs for use in electronic warfare, particularly tuneable properties or a wide absorption range to cover a large spectrum of frequencies, and enhanced directional properties in oriented or fibrous hexaferrites. These aerospace and defence needs are currently driving much of the research into more exotic forms of hexaferrites, as cost is much less of an issue for such applications. However, by its nature, most of this work is confidential or classified, and much is not published in the public domain.
There has been a recent increase in interest in the X and U ferrites, as they can be good MW absorbers in the X band (8–12 GHz). In an investigation of the Co$_{2-x}$Mn$_x$U system it was found that samples with a larger Mn content have good absorbing properties in the X band [247]. As can be seen in Fig. 71a, for $x = 1$ a maximum absorption of 98.84% ($-28.4$ dB) was seen at 8.5 GHz, with a level of >96% ($-14$ dB) over the whole X band (8–12 GHz). For $x = 1.5$ and 2 had multiple resonances over the X band (Fig. 71b), and $x = 2$ (Mn$_2$U) showed a strong absorption of $-20$ dB at 11.88 GHz (Fig. 71c), the same frequency at which a strong dielectric resonance and weak FMT was observed, indicating there may be coupling of these properties. In all of these U ferrites the optimum thickness for an absorber is 1.7 mm, allowing for the possibility of application as an absorbing paint. It has been shown that thermal spraying techniques such as atmospheric plasma spraying can be used to produce M ferrite RAM coatings [549]. For the Mn$_2$Zn$_x$U system, the general level of absorption was lower, with the Mn$_2$U sample again showing a very sharp absorption peak of 99% ($-20$ dB) at 11.98 GHz, very close to the sharp dielectric resonance peak (Fig. 71d). The Zn$_2$U sample (Fig. 71f) shows a strong absorption $>$90% for much of the X band, and has strong absorptions of $>$99% around 11.3–12.2 GHz, and the $x = 1$ sample has the strongest absorption of $>$98% throughout the X band, and 99.95% ($-33$ dB) at 122.3 GHz (Fig. 71e) [248]. When La was substituted for Ba in (Ba$_{1-3x}$La$_{2x}$)$_4$Co$_2$U ($x = 0.1$, 0.15 and 0.2), partial substitution of Ba$^{2+}$ by La$^{3+}$ enhanced electron hopping, which reduced magnetic interaction but led to wide band absorption in the X band. A peak absorption of $>$96% was measured for all values of $x$, with maxima of 99.8% at 8.5 GHz for $x = 0.1$ in a sample 1.5 mm thick and 99% at 10.2 GHz for $x = 0.2$ [249]. A similar level of absorption was seen in P$^{5+}$ substituted Ba$_4$(Co$_{1-5x}$P$_{2x}$)$_4$U ($x = 0–0.2$), and it was shown in both systems that by varying the thickness of the layer an absorbance of $>$96% could be tuned through the X band (Fig. 72), with thicker layers giving peak absorbance at lower frequencies [250]. This tuneable effect was strongest for fully P$^{5+}$ substituted Ba$_4$P$_{0.8}$La$_{1.2}$U ($x = 0.2$) and when 3 Ba$^{2+}$ had been substituted in Ba$_{1-3x}$La$_{2x}$Co$_2$U, where $\square$ = vacancy.

Co–Ni–P coated SrM nanopowder was reported to have an improved MW absorption (over $-10$ dB) across a wide bandwidth of 13.8 GHz between 5–20 GHz, with a Co$_{5}$Ni$_{40}$P$_{8}$ coating annealed at 400°C/1 h in N$_2$ [550]. The combination of MW and IR absorption shown by both BaM-BT ceramic composites and BaM-BT-PANI composites [484] reveals the potential for stealth and shielding materials that could disguise both radar and thermal imaging signatures in one composite or coating, and this is a fascinating area for future study.

![Fig. 71. Reflection loss spectra of Co$_{2-x}$Mn$_x$U for (a) $x = 1.0$ and (b) $x = 1.5$, (c) $x = 2$ [247], and of Mn$_{2-x}$Zn$_x$U for (d) $x = 0$, (e) $x = 1$ and (f) $x = 2$ [248], for different thicknesses of sample in mm.](www.iran-mavad.com)
12.6. Magnetoelectric (ME) and multiferroic (MF) applications

The great interest in ME and MF materials is the exploitation of the coupling between electric and magnetic properties. This could lead to a vast array of novel devices for applications such as dual electrical and magnetic field tuneable systems at MW and millimetre wave frequencies, miniature antennas, highly sensitive magnetic field sensors, activators and switches, high frequency signal processing devices (tuneable resonators, filters, inductors, phase shifters, delay lines and attenuators), gyrators and transformers, tuneable EM absorbers and RAM, wireless powering systems, transducers and energy harvesting [436,551]. To date, the effects seen in single phase MF materials are too weak for practical applications, and usually only operate at cryogenic temperatures, although the recently explored MF hexaferrites covered in this review hold potential for the future. Composite materials made of phases with excellent electrical (ferroelectric) and magnetic (ferro-/ferrimagnetic) properties can exhibit much stronger ME interactions, and already show great promise. There has been relatively little work carried out on hexagonal ferrites in this field so it is ripe for exploration, but devices consisting of YIG and a piezoelectric phase such as PZT, BT or BST have shown high ME coupling constants in the order of hundreds of V cm$^{-1}$ Oe$^{-1}$.

The enhancement of ME effects through resonance coupling also has great potential, especially at high-power GHz frequencies, and the low magnetic fields required also vastly increases the number of real-world applications. Non-ferrite ME composites have already been used to detect ac fields of $10^{-12}$ T and dc fields of $10^{-8}$ T [436]. They could also be used as current sensors or transformers, especially at resonance, where the voltage gain effect is greatly increased. Perhaps most importantly, all these effects can occur at ambient temperatures, especially in composites. There have recently been some excellent review papers on ME and MF composites [551,436], although not specifically for hexagonal ferrites.

One particular attraction is the electrical field or voltage tuneability of a ME material, as magnetic field tuning is often relatively slow, noisy and requires a lot of power. Electric field tuning is rapid, requires much less power, and would allow the miniaturization of such devices for integration into a chip or multilayer component. Such ME interactions are also enhanced around FMR frequencies, and $f_r$ can be tuned by the application of an electric field. Das et al. have recently published their findings on a PLD (pulsed laser deposition) produced multilayer ferrimagnetic-ferroelectric heterostructures with electrically tuneable FMR at GHz frequencies. This consisted of a 0.5 $\mu$m BaM layer on a sapphire substrate, with a 30 nm Pt layer on top, then a 10 nm MgO buffer layer, then a 4 $\mu$m BST layer, and topped with a 50 nm Pt layer, all produced at LTCC temperatures. This structure has a very low $H_A$, effective $H_A$ of 1273 kA m$^{-1}$ (16 kOe) and $M_s$ of 50 A m$^{-2}$ kg$^{-1}$, and $\varepsilon_r = 860$ at 100 kHz. $\varepsilon_r$ could be tuned down to 825 by applying $\pm 15$ V, and FMR frequency at 60 GHz could be shifted up by 30 MHz (500 ppm of $f_r$) with an applied voltage of 9 V, a tuneability of 3.5 MHz V$^{-1}$ [552].

Most of the composite ME hexaferrite research focuses on two kinds of composite structures: bonded bilayers, where an applied voltage causes a deformation in the piezoelectric phase that is coupled to a magnetic phase and shifts magnetic or FMR modes, and proximity effects in unbound dual phase composites, in which hybrid spin-EM waves are created. Such events are equally applicable.
in both thin film or bulk/thick film materials, and often the later can offer advantages as they are less affected by film-substrate induced strain effects. However, problems that need to be overcome in bulk ME composites are inhomogeneity, porosity, conductivity, defects, coherent interfaces between the phases, and interdiffusion during processing. Ideally, composites that co-sinter below LTCC temperatures are required for many device applications. Fibre-containing (1–3 type) and more complex geometry ME composite structures should also be investigated in the future. There will also be increasing interest in heterostructures and nanocomposites in the future. Techniques such as AFM, MFM, PFM and SQUID magnetometry are ideal for investigating such ME properties. A recently reported technique of interest is the scanning measurement and mapping of FMR by scanning probe microscope (FMR force microscopy), using an adapted MFM [553].

BSZY (Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Y) has another kind of ME coupling: magnetically rotatable ferroelectric polarisation. Kimura noted that a continuous rotation of the electrical polarisation can be achieved by changing the direction of an applied magnetic field. This is analogous to the electric field driven polarisation rotation seen in some ferroelectrics, such as PbZn$_{0.33}$Nd$_{0.67}$O$_3$-PbTiO$_3$, which could result in ultrahigh piezoelectricity. If the magnetic field is rotated through 360° in the hexagonal plane of BSZY, not only does the electric polarisation rotate as a function of cos $\theta$, but the magnetostriction rotates a function of cos $2\theta$, reaching a minimum when H is perpendicular to P, and a maximum when H is parallel to P (Fig. 73) [449]. A similar rotation of polarisation with H has been reported in Ba$_3$Mg$_2$Y. although strong up to field of 1T when rotating in the plane, the effect had decayed greatly at fields of 0.1 T, and showed no effect at 1 T, when rotating perpendicular to plane (Fig. 73), due to the anisotropy involved [554]. This gives rise to potential applications exploiting the coupling of ME and optical properties (magneto-electrical–optical effect), analogous to the Kerr effect.

12.7. Other applications

Various designs for sensors incorporating ferrites have been proposed, including a humidity sensor based upon the change of resistance in a copper–zinc ferrite [555]. A device has been proposed, con-

![Fig. 73](Image)

**Fig. 73.** Left: Electric polarisation rotation accompanied by magnetostriction in Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$. (a) electric polarisation and (b) magnetostriction against magnetic field angle, at $H = 1$ T and temperature of 20 K. Solid curves are fit to the function (a) cos $\theta$ and (b) cos $2\theta$ [449]. Right: Polarisation of Ba$_3$Mg$_2$Y as a function of the rotation angle $\phi$ of magnetic field with respect to the [001] direction and the rotation angle $\theta$ of magnetic field with respect to the [120] direction. The magnetic field rotates horizontally (a–d) and vertically (e–h) in the shaded planes shown in (a and e) [554].
sisting of a uniaxial hard ferrite wire or fibre, made with the anisotropy along the wire's axis, with a conducting coil wound around it and a BaM magnet at each end, which could detect 0.7 mV per turn of wire in the coil [556]. A highly porous BaM was made by the citrate process at 900 °C, doped with 1–5 wt.% Ir$^{3+}$, which stabilised the high surface area up to 1200 °C. The material was found to be a good catalyst for the clean combustion of methane [557]. Hexaferrites can also find medical applications, for example as components in nuclear magnetic resonance imaging and magnetomotive biomedical implants, but the toxicity of some of the component elements, particularly barium, limits their use in applications where they must be inserted into the human body as particles or fluids. Micron sized SrM grains have been surface modified with oleic acid to improve their dispersity in water with almost no loss of magnetisation, and these were subsequently treated with oleic acid to make large (500–900 µm) polymeric microspheres with a magnetic core, that should be biocompatible (Fig. 74) [182]. Co$_2$Z coated MFM cantilevers have been used to give improved high-frequency measurements compared to standard CoCr coated tips, performing imaging up to 2 GHz with resolution of 20 nm [558]. This could be of particular interest to industry for the imaging, characterisation and quality control of high density magnetic discs drives and recording heads at high frequencies. Although unsuitable for uses as magnets, SrFe$_{12-x}$Al$_x$O$_{19}$ with high levels of Al substitution are promising for millimetre wave imaging, which can be used to penetrate aerosols, dust and fabric, and has obvious security applications [191].

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