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## Low-temperature wet chemistry synthetic approaches towards ferrites\*

Stefano Diodati,<sup>a</sup> Richard I. Walton, <sup>b</sup> Simone Mascotto <sup>c</sup> and Silvia Gross <sup>\*</sup>

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Ferrites are a broad class of iron-containing oxides that includes spinel ferrites MFe<sub>2</sub>O<sub>4</sub>, perovskites  $MFeO_{3}$ , and hexagonal ferrites (hexaferrites) such as BaFe<sub>12</sub>O<sub>19</sub>. These materials have a wide array of applications owing to their diverse properties: notable instances include catalysis, piezoelectric components, magnetic components, biomedical applications, heterogeneous catalysis and photocatalysis. Given the growing importance of environmentally friendly, low-temperature methodologies to obtain functional materials, there is a growing interest in synthetic approaches which are compatible with the principles of "green chemistry". In this context, wet chemistry represents an attractive choice, and furthermore offers the possibility of scale-up for manufacture of materials in volumes for practical application. Though there is a sizeable amount of literature on the synthesis of ferrites, the most common approaches require treatments at temperatures above 200 °C, either as the main synthetic procedure itself (thermal decomposition), or as a post-synthetic step (for example, calcination after sol-gel autocombustion). This review aims at summarising, categorising, classifying and critically discussing the different low-temperature (<200 °C), wet chemistry approaches employed in recent years for the synthesis of ferrites. This will include hydrothermal, solvothermal, sonochemical, and microwave methods, with examples taken from literature making reference to the various sub-classes of ferrites.

## Ferrites: a useful and multifaceted class of compounds

Ferrites are a broad class of oxides containing iron which in general include spinel ferrites MFe<sub>2</sub>O<sub>4</sub>, perovskites, ilmenite (FeTiO<sub>3</sub>) and hexagonal ferrites (or hexaferrites). These materials have a wide array of applications owing to their diverse properties.<sup>1-10</sup> Notable examples include catalysis,<sup>11-15</sup> piezoelectric components,<sup>16,17</sup> magnetic components,<sup>18–21</sup> bio-medical applications<sup>22,23</sup> and photocatalysis,<sup>24–29</sup> photoanodes<sup>30</sup> and photocathodes.<sup>31</sup> In particular, their magnetic properties make them convenient materials for heterogeneous catalysis as they greatly simplify catalyst isolation and recovery operations. In general, the nature of ferrites as iron-containing oxides endows them with important magnetic properties, which vary depending on the specific structure and nature of non-iron metals involved.<sup>32,33</sup> Spinels in particular (due to

their specific structure - vide infra) have been shown to display both hard  $(CoFe_2O_4)^6$  and  $soft^{33}$  magnetic behaviour, making them very attractive materials in applications ranging from magnetic recording to magnetic resonance imaging (MRI).<sup>6,34,35</sup>

Given the importance of ferrites in a wide variety of fields, numerous works have been dedicated to the synthesis and study of these materials.<sup>1,3,18,33,34,36-46</sup> The present review will, however, focus specifically on wet chemistry methods which not only afford the desired materials, but also comply with the principles of Green Chemistry47 and can be achieved whilst maintaining low temperatures ( $\leq 200$  °C) of synthesis, due to the importance for industry to steadily move towards greener and more environmentally friendly approaches (vide infra "Green chemistry: the need for low-temperature wet synthesis approaches").

#### Spinels

In general, spinel ferrites can be described as ferrites having the formula MFe<sub>2</sub>O<sub>4</sub>, where M is a divalent metal species (such as Fe, Co, Zn, Ni Cu or others).<sup>32,48–51</sup> From a crystallographic point of view, spinel ferrites crystallise in a cubic close-packed structure<sup>32,34</sup> having  $Fd\bar{3}m$  symmetry with a unit cell containing 8 formula units (M<sub>8</sub>Fe<sub>16</sub>O<sub>32</sub>).<sup>21,34</sup> In particular, metal ions within this structure occupy 1/8 of the tetrahedral and 1/2 of the octahedral sites.<sup>32,48-50,52</sup> Spinel structures are divided

<sup>&</sup>lt;sup>a</sup>Dipartimento di Scienze Chimiche – Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italy. E-mail: silvia.gross@unipd.it

<sup>&</sup>lt;sup>b</sup>Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry, CV4 7AL. UK

<sup>&</sup>lt;sup>c</sup>Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

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between normal, inverse and partially inverse spinels. In normal spinel ferrites (such as for instance  $\text{ZnFe}_2O_4$ )<sup>53</sup> the trivalent metal (*i.e.* Fe) occupies octahedral sites, whereas the divalent metal ions (Zn) lie in tetrahedral sites (Fig. 1). A second class of spinels are known as inverse spinels (such as NiFe<sub>2</sub>O<sub>4</sub>);<sup>52</sup> in inverse ferrites the iron cations are equally split between tetrahedral and octahedral sites, whereas the divalent atoms occupy in turn the octahedral sites vacated by iron.

A third (much broader) subset of spinels exists where the structure is intermediate between normal and inverse, these are known as partially inverse spinels. In general, therefore, the chemical formula for a spinel ferrite may be written as  $[M_{1-i}Fe_i]^{\text{TET}}(M_iFe_{2-i})^{\text{OCT}}O_4$  where the square and curved brackets labelled TET and OCT represent the tetrahedral and octahedral environments of the ions, respectively and *i* (where  $0 \le i \le 1$ ) is known as degree of inversion (with 0 indicating a normal and 1 indicating an inverse spinel ferrite structure).<sup>52</sup>

This distinction is very important because many of the particular properties which make spinel ferrites such interesting functional materials arise directly from this distribution of metal species over crystal sites.<sup>52,54–58</sup> Many studies have been carried out on how to control the cation distribution in spinels to affect the final properties of the resulting material.<sup>52,54–56,58</sup> While bulk ferrites have a typical degree of inversion, depending on the nature of the M metal, the value of i in nanosized ferrites may vary based upon the synthetic history of the material; in particular, low temperature synthesis may allow access to a different distribution of cations than can be accessed at high temperatures.<sup>54,58–60</sup>

A subclass of spinel ferrites includes more than one metal. These "doped" or "quaternary" ferrites  $M_xM'_{1-x}Fe_2O_4$  can therefore take advantage of the properties of both "parent ferrites" (MFe\_2O\_4 and M'Fe\_2O\_4).<sup>19,42,61-67</sup> Because each M species



Fig. 1 Crystal structure of normal spinel ferrite  $ZnFe_2O_4$  highlighting the octahedral Fe (blue) and tetrahedral Zn sites (green) with red oxide anions.

has its own characteristic electronic structure, the oxides may feature novel or enhanced properties.<sup>68–71</sup>

This great variety of structural and compositional possibilities endows spinel ferrites with a very broad spectrum of magnetic, electric and functional properties,<sup>6,55,56,72–75</sup> making them materials of great interest in a high number of applicative avenues. Nickel and magnesium ferrites have been reported as potential catalysts for water splitting and CO<sub>2</sub> decomposition.<sup>25,76</sup> The magnetic properties of spinel ferrites have furthermore attracted interest in the fields of spintro-



Stefano Diodati

Stefano Diodati is a postdoc fellow in the workgroup of Prof. Silvia Gross. His field of research concerns the synthesis of crystalline inorganic nanostructures (ferrites, oxides, sulphides) through wet chemistry methodologies, with a particular focus on low temperature, green methods such as subcritical hydrothermal synthesis. A further focus of his research is the characterisation of inorganic materials from the compositional

(XPS, ICP-MS), structural (powder XRD) and morphological (SEM, AFM) point of view. Most recently he worked on the statistical characterisation of coffee extracts through comparative NMR and other complementary techniques.



organic materials, focussed on the use of innovative synthesis methods for functional solids. This spans zeotypes and metalorganic frameworks through to condensed oxides, with an emphasis on solution-based synthesis routes and characterisation using diffraction and spectroscopy including at synchro-

Richard Walton is Professor of Chemistry at the University of

Warwick and his research group

is working in the field of in-

**Richard I. Walton** 

tron and neutron facilities. Practical applications are explored and exploited through various industrial collaborations including in areas such as heterogeneous catalysis and ionic conductors. He is presently an editor of the Inorganic Materials Series published by the Royal Society of Chemistry.

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nics<sup>77</sup> and biomedicine,<sup>78–81</sup> where they can act as either drug carriers or as *foci* for hyperthermia treatments. Spinels have further found applications in the fields of sensors,<sup>82,83</sup> magnetic adsorbers,<sup>21,84</sup> antiparasitic agents<sup>85</sup> and as components for magnetic devices.<sup>86–88</sup>

#### Perovskites

The ABX<sub>3</sub> perovskite structure is one of the most familiar and versatile found in solid-state inorganic materials.<sup>89</sup> Named for the mineral CaTiO<sub>3</sub>, the perovskite structure is adopted by many possible combinations of cations (A and B) and anions (X). The A cation adopts coordination number 12 in the ideal cubic perovskite, while the smaller B cation adopts octahedral coordination, such that a three-dimensional network of corner-shared [BX<sub>6</sub>] octahedra form a network in which the larger A cations reside, Fig. 2. The versatility in the structure lies in its structurally flexibility: distortions of the structure are possible to accommodate a range of relative ionic sizes, the most common of which are concerted rotations of the cornershared octahedral to maintain their connectivity, while lowering the coordination number of the A-site cations, Fig. 2b. Another often found distortion is displacement of the B-site cations within their octahedra. This can give rise to polar properties, exploited in ferroelectric devices. For ABO<sub>3</sub> oxides, various combinations of differently charged cations are possible to ensure neutrality: commonly A<sup>3+</sup>B<sup>3+</sup>O<sub>3</sub>, A<sup>2+</sup>B<sup>4+</sup>O<sub>3</sub> and  $A^{+}B^{5+}O_{3}$ . Thus for iron in ferrites, the composition  $A^{3+}Fe^{3+}O_{3}$ is expected to be prevalent, with the expectation that replacement of A<sup>3+</sup> by A<sup>2+</sup> may permit partial oxidation of the Fe to the higher +4 oxidation state.

Ferrite perovskites have attracted interest for their various properties and continue to be heavily researched. Magnetic properties have long been studied in this family, in particular



Fig. 2 The ABX<sub>3</sub> perovskite structure (a) view of ideal cubic unit cell with blue  $[BX_6]$  octahedral and green 12-coordinate A sites and (b) the distorted orthorhombic unit cell as found for GdFeO<sub>3</sub> where the octahedral are tilted with respect to each other.

in the rare-earth ferrites (so-called orthoferrites), where A is a lanthanide or Y<sup>3+</sup> and B is Fe<sup>3+</sup>.<sup>90</sup> Depending on the rare-earth cation the materials show complex magnetic behaviour associated with orientation of spins of each of the lanthanide and Fe<sup>3+</sup> sub-lattices. More recently the interplay of magnetism and polar properties has emerged of being importance.<sup>91</sup> Such multiferroicity and enhanced magnetoelectric coupling in ferrites is exemplified by BiFeO3 that has been the focus of intense investigation in this respect.92-94 The coexistence of coexistence of ferroelectricity, ferroelasticity, and ferromagnetism in a single phase is of relevance for the development of electronic devices such as in next generation data storage and BiFeO<sub>3</sub> shows antiferromagnetism, ferroelectricity and ferroelasticity over a wide temperature range above room temperature. Photocatalysis by BiFeO<sub>3</sub> has also been widely studied, due to its band gap being appropriate for solar light activation, and it has been thoroughly investigated for the degradation of organics in solution.<sup>95</sup> The hexagonal ferrite perovskites of the



Simone Mascotto

Simone Mascotto (1981, Trento, Italy) is Assistant Professor of Inorganic Chemistry at the University of Hamburg, Germany. He received a MSc degree in Industrial Chemistry from the University of Padua (2006) and a PhD in Physical Chemistry from the Justus-Liebig-University of Giessen (2009). In 2010–2013 he was a Marie Curie postdoctoral fellow at the University of Trento, Italy and research associate at the

Helmholtz-Zentrum Berlin, Germany. His research group focuses on the design of metal oxides with tailored surface properties and on the investigation of surface-related phenomena in nanomaterials by scattering methods at large scale facilities.



Silvia Gross

cal and chemico-physical characterisation of the materials, also by time-resolved and/or in situ experiments performed at synchrotron radiation sources. She is DFG Mercator Fellow and regularly visiting professor at the Justus-Liebig University of Giessen. She has authored about 160 ISI papers.

Silvia Gross is Professor of Inorganic and Colloid Chemistry

at the University of Padova and

her research group is working in

the field of wet-chemistry and

colloidal synthesis of different

inorganic materials (oxides, sul-

phides, metal nanoparticles), with particular focus on low

temperature and sustainable

routes. A relevant part of the

activity is devoted to the

thorough structural, morphologi-

smaller rare earths (Y, Dy–Lu) have also been recently studied for their multiferroic properties.<sup>96</sup>

Ferrite perovskites have shown promise as heterogeneous catalysts for oxidation reactions, and have been investigated for many years,<sup>97</sup> in applications such as methanol oxidation.<sup>98,99</sup> With an increasing interest and awareness of environmental concerns and the need for effective catalysts for clean combustion and pollution abatement, the materials continue to be developed and optimised for applications. La<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3</sub> materials have been shown to be effective for activation of the combustion of propane and ethanol, which was ascribed to the presence of Fe<sup>4+,100</sup> A systematic study of AFeO<sub>3</sub> (A = La, Nd, Sm) and  $LaFe_{1-x}Mg_xO_3$  found that the materials gave complete conversion of methane and CO, with a correlation between structural chemistry, chemical composition and activity.<sup>101</sup> More detailed studies of non-stoichiometry in  $La_{1-x}FeO_{3-\delta}$  showed that composition dictates activity for hydrocarbon oxidation,<sup>102,103</sup> while others have also suggested that the synthesis method is also important.<sup>104</sup> Wet chemical approaches have been shown to give higher surface area for LaFeO<sub>3</sub>.<sup>105</sup> This enables LaFeO<sub>3</sub> to be used as a support for precious metals to perform effective oxidations.<sup>106,107</sup>

Other recent examples of catalysis applications include LaFeO<sub>3</sub> for activating  $H_2O_2$  to oxidise methyl orange,<sup>108</sup> in three-way catalysis for automotive exhausts,<sup>109</sup> for the conversion of CO and NO to dinitrogen,<sup>110</sup> and a titanium-doped LaFeO<sub>3</sub> has been used for catalytic wet peroxide oxidation.<sup>111</sup> Electrocatalytic activity towards oxygen evolution in alkaline media has been long studied with ferrites since systematic work on La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3- $\delta$ </sub>,<sup>112,113</sup> and has been tuned by exploring structure–property relationships in much more complex solid-solutions.<sup>114</sup> This is of tremendous importance in contemporary applications in rechargeable batteries, fuel cells, and hydrogen production from water splitting.

Other important applications of orthoferrites are as cathode materials in solid-oxide fuel cells: here mixed ionicelectronic conductors are needed, along with catalytic activity for oxygen reduction and thermal expansion that is matched to a solid electrolyte.<sup>115,116</sup> To meet this combination of criteria, substitutions into the parent LaFeO<sub>3</sub> perovskite has been extensively studied to tune the electronic structure and to induce oxide-ion vacancies to provide anion conduction pathways. This includes materials co-doped with Sr and Ni, or  $\text{Co.}^{117,118}$  The material  $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{FeO}_{3-\delta}$  when doped at the B-site with Cu, Ni or Co has proved to be compatible with proton-conducting electrolytes.<sup>119</sup> Related to this, is recent work that shows how the oxygen non-stoichiometry in ferrites can be used for thermochemical air separation, making use of their intrinsic oxygen storage capacity, such as in  $SrFe_{0.95}Cu_{0.05}O_{3-\delta}$ ,<sup>120</sup> or the parent  $SrFeO_{3-\delta}$ .<sup>121</sup>

#### **Hexagonal ferrites**

The  $ABX_3$  composition is found in other structure types, which are often labelled as perovskites, but these do not have the essential feature of solely corner-shared octahedral  $[BX_6]$  units.

For example, Fig. 3a and b shows the structure of an example of a so-called 'hexagonal perovskite' that contains layers of corner-linked  $[BX_6]$  trigonal bipyramids, separated by layers of A cations.<sup>122</sup> This structure is found for some ferrites, notably ferrites of the small rare-earth cations, as will be discussed below.

A second important type of hexagonal ferrite are the 'hexaferrites' exemplified by the barium iron oxide  $BaFe_{12}O_{19}$ . This phase, known as the M-type hexaferrite, has a structure containing iron in three distinct coordination environments, octahedral, tetrahedral and pyramidal, Fig. 3c. More complex hexaferrite structures are known, such as the Y-type  $Ba_2Me_2Fe_{12}O_{22}$ , where Me is a divalent metal cation, and the family is further diversified by stacking of M-type, Y-type and spinel motifs.<sup>36</sup>

The hexaferrites have long been studied for their magnetism, which find widespread technological used in hard permanent magnets in applications such as magnetic recording and data storage materials, but they are also now used as components for mobile and wireless communications at microwave per GHz frequencies, and in electromagnetic wave absorbers.<sup>1</sup> Recent interest has been focussed on the formation of composite materials based on hexaferrites, such as with polymer matrices, and for this purpose fine powders of the oxides are needed that can be suitably surface modified.<sup>123</sup>

# Green chemistry: the need for low-temperature wet synthesis approaches to ferrites

From a functional and applicative point of view, ferrites are becoming increasingly relevant. As outlined at the beginning of this review, new application avenues have been disclosed in an endeavour to enhance both the economic and the environ-



**Fig. 3** Example of hexagonal ferrites (a) and (b) shows the ABO<sub>3</sub> hexagonal layered perovskite structure as found for YbFeO<sub>3</sub> (YMnO<sub>3</sub> type), where [BX<sub>5</sub>] trigonal bipyramids are shown in blue and layers of A cations are the green spheres: (a) view showing stacking of layers and (b) a view perpendicular to the layers. (c) shows the unit cell of the hexaferrite BaFe<sub>12</sub>O<sub>19</sub> with three distinct iron environments: octahedral (red), tetrahedral (yellow) and pyramidal (orange) and 12-fold coordination sites for Ba (blue).

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mental sustainability of synthetic approaches, thus also complying with one of the most relevant out of the 12 paradigms of Green Chemistry:<sup>47</sup> lowering processing time and temperature, which would allow to pursue the goal of reducing energy consumption, a goal which in turn represents one of the major targets in designing future sustainable syntheses of materials.

Lowering temperatures necessarily requires a turn to wet chemistry and solution-based routes, since temperatures below 200 °C are not sufficient to reach the activation energy required for solid state reactions, grain coalescence and coarsening, and eventually the initiation of crystallisation in solid state. In wet-chemistry routes, the limit imposed by the boiling point of the used medium or solvent inherently helps maintain milder synthesis conditions. Despite some exceptions (e.g. polyol synthesis<sup>124</sup> and the Pechini<sup>125</sup> method), most of the currently used wet chemistry routes affording the crystallisation of inorganic nanostructures are carried out at temperatures ranging from room temperature (e.g. mini- and microemulsion, biogenic synthesis, radiolysis, sonolysis, laser ablation, microfluidics) to 150-200 °C (sol-gel, hydro- and solvothermal, coprecipitation), only rarely exceeding them. There is still space for improvement: the experimental set-up can be optimised to increase the efficiency of the heat and mass transfer during the synthesis, as well as to reduce heat losses, making the overall process more energy efficient.

It should however be pointed out that lowering the synthesis temperature, is not the only relevant aspect involved in reducing the energy consumption: decreasing the processing time, *i.e.* the time for which energy must be provided to the reaction system, is also of paramount important. A systematic optimisation of the experimental landscape is needed for this aspect as well. A recent work by some of us<sup>126</sup> has shown how the crystallisation of ferrites by an already established hydrothermal approach,<sup>127</sup> relying on heating a suspension of oxalates at 135 °C for 24 h, could be also achieved by heating for only 1 to 3 hours (depending on the nature of the involved divalent metal cation), which implies a reduction in energy consumption, all other conditions being equal, by a factor of 24 to 8. In this work, the crystallisation of the targeted ferrites was followed, in a time-resolved fashion, by using different analytical tools sensitive to different range orders, from local/ atomic (XAS, XPS) to long range (XRD, SAXS) to macroscopic scale (TEM, SEM). It could furthermore be pointed out that the nucleation and growth of the final nanostructures occurs within a very limited time frame, and no further growth occurs by increasing the heating period.

# Hydro/solvothermal approaches to ferrites

The term hydrothermal refers to the use of water as a reaction medium when heated to above its boiling point in a sealed vessel. Under these conditions, autogeneous pressure is produced, and the combined role of increased temperature and pressure in the synthesis and crystallisation of solids has been long studied.<sup>128,129</sup> It is already known how under these conditions, physical properties of water, such as viscosity, ionic product and dielectric constant, change significantly at high pressure and temperature thus enabling solubilisations, crystallisations and, possibly, chemical reactions that would not occur under normal conditions. This is particularly the case once the supercritical point is exceeded (for water  $T_{c}$  = 647.14 K and  $p_c = 22.06$  MPa), but even so most hydrothermal reactions currently reported use milder conditions. The term solvothermal, later coined by Demazeau,<sup>130-132</sup> encompasses all possible solvents, with their differing boiling points, viscosities and dielectric constants, and this method widened the use of solution chemistry to allow access to a larger range of materials. These solution-based routes to solids originally developed from studies of the formation of minerals in the Earth's crust and led to synthetic silicates, exemplified by the zeolites.133 The growth of large crystals of a range of materials has benefitted from hydrothermal chemistry,<sup>134</sup> and more recently attention has turned to the formation of polycrystalline powders of condensed solids that would usually be prepared using the high temperatures associated with solid-state chemistry.<sup>135-141</sup> The ongoing use of hydrothermal chemistry is also driven by the discovery of new materials, with compositions and structure types not seen by other preparative routes, and that may be metastable under conventional synthesis conditions,<sup>142</sup> as well as control over crystal form over length-scale from nanometres upwards.<sup>143</sup> The key feature of the hydro/solvothermal method is that synthesis and crystallisation of a materials occurs in a single reaction, directly from solution, with no second step of annealing or calcination need to induce the formation of the desired phase. This then means that intricate crystal forms can be isolated, or metastable atomic-scale structure and polymorphs, that would otherwise transform or collapse at elevated temperature. Most solvothermal chemistry for materials synthesis is performed under rather mild conditions, with maximum temperature of around 250 °C, so the pressure generated is not high (typically ten times atmospheric pressure) and arguably not an important synthetic parameter, but under these conditions reagents that would otherwise be insoluble are solubilised to some extent (often with the aid of a mineraliser) to bring about crystallisation from homogeneous solution or to mediate heterogeneous reactions. While some authors report the use of solvothermal chemistry as a processing step, which is followed by a high temperature annealing rather like sol-gel chemistry, in the following sections we will focus on true solvothermal synthesis, where the advantages outlined above are at play. We have chosen examples of materials to show the versatility of the hydrothermal method: this includes a range of chemical compositions and also materials whose properties have been characterised for practical applications.

#### Solvothermal routes to perovskites

In this section we will review the solvothermal crystallisation of  $AFeO_3$  materials, where A = a large trivalent cation. In terms

of ferrite perovskites, much work has been done on the hydrothermal crystallisation of BiFeO<sub>3</sub>, which has been the focus of attention for its multiferroicity and, more recently, its photocatalytic properties.<sup>95</sup> There are numerous published reports of the one-step hydrothermal crystallisation of the solid in the past 12 years, and many examples are summarised in Table S1 (ESI),† which contains selected examples of the published work on this chemistry. Chen et al. in 2006 pioneered this work, reporting the phase-pure synthesis of BiFeO<sub>3</sub> as submicron crystallites from aqueous 4 M KOH.<sup>144</sup> The same year, Han et al. reported that, along with BiFeO<sub>3</sub>, two further bismuth ferrites could be selectively synthesised as phase-pure powders: the sillenite-structured Bi<sub>12</sub>Fe<sub>0.63</sub>O<sub>18.945</sub> (close to the ideal composition Bi<sub>25</sub>FeO<sub>40</sub>) and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>.<sup>145</sup> As well as phase selectivity the crystal morphology could be adjusted by temperature and/or pH as shown in Fig. 4. This illustrates the complexity in hydrothermal synthesis if competing phases form from a given set of reagents and shows how optimisation of conditions may be necessary to obtain a desired phase as a pure material.

Li *et al.* later tuned the crystal form of  $BiFeO_3$  on the micron-scale by choice of pH and introduction of a polymer (polyethylene glycol) to the synthesis, as shown in Fig. 5.<sup>146</sup>

Table S1 in ESI<sup>†</sup> shows the frequent observation of competing sillenite  $Bi_{25}FeO_{40}$  and  $Bi_2Fe_4O_9$  materials in the hydrothermal synthesis of BiFeO<sub>3</sub>. The formation of these may depend on the Bi: Fe ratio used in the synthesis, but Cai *et al.* proposed that  $Bi_{25}FeO_{40}$  is formed early in the hydrothermal



Fig. 4 SEM images of bismuth ferrites prepared by hydrothermal synthesis (A) Bi<sub>12</sub>Fe<sub>0.63</sub>O<sub>18.945</sub> (pH ~ 12, heating temperature, 180 °C); (B) Bi<sub>12</sub>Fe<sub>0.63</sub>O<sub>18.945</sub> (pH ~ 10, 180 °C); (C) Bi<sub>12</sub>Fe<sub>0.63</sub>O<sub>18.945</sub> (pH ~ 8, 180 °C); (D) BiFeO<sub>3</sub> (200 °C); (E) Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> (180 °C); (F) Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> (270 °C). Reprinted with permission from Han *et al.*<sup>145</sup>



Fig. 5 Crystal morphology control of BiFeO<sub>3</sub> proposed by Li *et al.* and reproduced with permission.<sup>146</sup>

reaction and reacts further to give the perovskite product; in their case, the stabilisation of the sillenite was aided using polyvinylalcohol as an additive in solution.<sup>147</sup> Lopes *et al.* performed a detailed study that supported this view, showing that  $Bi_{25}FeO_{40}$  could be formed at room temperature, and then under hydrothermal conditions was formed at short reactions times before the emergence of  $BiFeO_3$ .<sup>148</sup>

While most of the work on BiFeO<sub>3</sub> has used hydrothermal conditions (*i.e.* water as solvent) there is some evidence how the presence of a secondary solvent can influence the crystallisation and hence form of the products. For example, Chen *et al.* found that the addition of acetone lowered the synthesis temperature,<sup>149</sup> while Zhang *et al.* found that addition of polyvinylpyrrolidone in ethanol lead to the assembly of primary crystallites into a hierarchical structure of micron diameter rods.<sup>150</sup>

Hou *et al.* performed hydrothermal synthesis of BiFeO<sub>3</sub> in an applied magnetic field and found that with increasing field strength up to 12 T the crystallite size decreased from 40  $\mu$ m to 20  $\mu$ m and at 12 T chain-link agglomerates of the primary particles were formed, Fig. 6.<sup>151</sup> The subsequent magnetic response of the materials was improved for the samples pre-



**Fig. 6** SEM images of BiFeO<sub>3</sub> obtained by hydrothermal synthesis at 200 °C with 8 M KOH for 6 h in various magnetic fields: (a) 0 T; (b) 4 T; (c) 8 T and (d) 12 T. Reproduced with permission from Hou *et al.*<sup>151</sup>

pared in-field: magnetisation measured under a 1.8 T magnetic field was enhanced from 0.1003 emu  $g^{-1}$  (0 T) to 0.2067 emu  $g^{-1}$  (12 T).

The hydrothermal method can be used to crystallise films of oxides on suitable substrates and in the case of BiFeO<sub>3</sub>, Huang *et al.* showed how epitaxial growth of the material on orientated surfaces of SrTiO<sub>3</sub> was possible to give micron-thick films with favourable dielectric properties.<sup>152</sup> This is important for the fabrication of electronic devices, but annealing is necessary to remove and achieve the dielectric properties expected for the material.

Substitutional chemistry of BiFeO<sub>3</sub> using hydrothermal crystallisation is also possible in one-step hydrothermal reactions, and this has been done to tune dielectric and ferromagnetic properties. The advantage of the solution mediated reaction is a high homogeneity of atomic mixing, which by solid-state synthesis often requires repetitive cycles of grinding and heating to achieve. Lanthanum-doped BiFeO<sub>3</sub> materials,  $Bi_{1-x}La_xFeO_3$  with x up to 0.3 have been reported from hydrothermal reactions, with enhanced ferromagnetic and dielectric properties over the parent material,<sup>153,154</sup> whilst using microwaves as the heating source allowed rapid synthesis of materials with even higher lanthanum content.155 Replacement of Bi<sup>3+</sup> by Ba<sup>2+</sup> is also possible,<sup>156</sup> while codoping with both Ca<sup>2+</sup> and Sm<sup>3+</sup>, leads to oxide-ion vacancies as seen by XPS, which may be responsible for the high temperature dielectric anomalies observed in the material.<sup>157</sup>

The extensive work on the hydrothermal synthesis of BiFeO<sub>3</sub>, clearly illustrates its ease of implementation over a range of pH, temperature, reaction time, with some choices of reagents possible. In contrast, hydrothermal synthesis of rareearth (lanthanide, yttrium or scandium) ferrites has received comparatively less attention. Yoshimura and co-workers reported in the 1980s that the hydrothermal synthesis of LaFeO<sub>3</sub> required temperatures above 300 °C from lanthanum oxide and hydrated iron oxide in KOH solution, with optimum temperature 450-500 °C.<sup>158</sup> This has been verified by Adschiri and co-workers.<sup>159</sup> More recent work has shown how additives in solution can bring about hydrothermal crystallisation of LaFeO<sub>3</sub> from nitrate precursors KOH solution at around 250 °C. The additives include sodium carbonate,<sup>160</sup> urea,<sup>161,162</sup> and while others have used citric acid, although a second step of calcination at 800 °C is needed in those cases to crystallise the materials, so these are not strictly hydrothermal reactions but more akin to a co-precipitation.<sup>163,164</sup> Interestingly, the rare-earth ferrites of other lanthanides are more readily synthesised: this includes those of all of the elements Pr-Lu (except Pm) that crystallise at 240 °C from KOH in 24 hours without any need for extra mineralisers or additives; the materials are highly crystalline and have magnetic properties that match those prepared by conventional solid-state synthesis.<sup>165–169</sup> In the case of YbFeO<sub>3</sub>, the choice of mineraliser, KOH, NaOH, or mixtures of, was shown to influence crystal morphology, which was rationalised by considering the interaction of solution cations with the growing phases of the crystallites: as shown in Fig. 7, one effect is to adjust the



Fig. 7 SEM images of orthorhombic YbFeO<sub>3</sub> with NaOH/KOH mixed mineraliser: (a) 25 M/0 M; (b) 20 M/5 M; (c) 15 M/10 M; (d) 10 M/15 M; (e) 5 M/20 M; and (f) 0 M/25 M. Reproduced with permission from Zhang et al.<sup>170</sup>

aspect ratio of the cuboid crystals that are formed.<sup>170</sup> B-Site doping has also proved possible in the series LaFe<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> ( $0 \le x \le 1$ )<sup>171</sup> and REFe<sub>0.5</sub>Cr<sub>0.5</sub>O<sub>3</sub> (RE = La, Tb, Ho, Er, Yb, Lu and Y)<sup>172</sup> prepared directly from hydrothermal solutions at 240 °C in aqueous KOH and their magnetic and ferroelectric properties shown to be highly dependent on composition. Similarly, the series GdFe<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> ( $0.1 \le x \le 0.9$ ) has been prepared and characterised.<sup>173</sup>

The rare-earth ferrite YFeO<sub>3</sub> also crystallises directly from solution and although some groups have reported that higher temperatures of 300 °C are needed,<sup>174–176</sup> others have used 240 °C and concentrated KOH.<sup>177</sup> The fact the some of the rare-earth orthoferrites require high temperature (supercritical) hydrothermal conditions or the use of additives is not understood at present. Feng and co-workers proposed that the role of urea as additive was to release NH<sub>4</sub><sup>+</sup> into solution where it interacted with the growing faces of the perovskite crystals.<sup>161,178,179</sup> Further work is needed to prove this hypothesis and to understand properly the kinetics and mechanism of crystal growth of perovskites from hydrothermal solutions.

For the smaller rare-earth cations, a hexagonal perovskite structure is also possible (see Fig. 3 above) and this may be accessed using solvothermal synthesis selectively over the orthorhombic polymorph. For example, the reaction between rare-earth (RE) acetates (RE = Tm–Lu) and iron acetylacetonate in 1,4-butanediol at 300 °C gave hexagonal REFeO<sub>3</sub> materials consisting of submicron particles.<sup>180</sup> Upon subsequent calcination, the hexagonal phases irreversibly transformed into the perovskite phase at around 980 °C. This is an important example of how the use of mild synthesis conditions allows accessible to a metastable polymorph that cannot be stabilised at high temperature by classical solid-state synthesis. In the case of YbFeO<sub>3</sub>, the solvothermal reaction between Yb chlorides and iron acetylacetonate in 1,4-butanediol in the presence of 1,6-hexanediamine yielded the orthorhombic perovskite YbFeO<sub>3</sub>, in contrast to the hexagonal polymorph prepared using the prior method.<sup>181,182</sup>

As well as the perovskites, it is here worth mentioning that FeTiO<sub>3</sub>, the mineral ilmenite, can be prepared via hydrothermal synthesis. Although having a perovskite-like composition, this material has a trigonal corundum structure with alternating layers of octahedral Fe<sup>2+</sup> and Ti<sup>4+</sup>. Guan et al. prepared hexagonal plates of FeTiO<sub>3</sub> hydrothermally and tested their electrochemical and catalytic properties,<sup>183</sup> Zhang et al. prepared various morphologies at 180 °C, depending on reaction time and solution pH, and demonstrated shape-dependent photocatalysis for the degradation of an organic dye,<sup>184</sup> Aparna and Sivasubramanian used a urea-aided hydrothermal method to prepare hexagonal plates (300 nm diameter) that could be as electrochemical sensors for dopamine,<sup>185</sup> and Palanisamy et al., prepared nanoflower-shaped particles that were tested as a catalyst for electrochemical CO<sub>2</sub> reduction.<sup>186</sup> Tao et al. used a different approach for preparing FeTiO<sub>3</sub> nanostructures, by ball milling commercially available FeTiO<sub>3</sub> followed by hydrothermal treatment.187,188

#### Hydro/solvothermal approaches to spinels

In this section we will consider spinels consisting of divalent cations in combination with trivalent Fe. The spinels MFe<sub>2</sub>O<sub>4</sub> (M = Mn, Co, Ni, Cu, Zn, Mg) are the most widely studied and form readily under hydrothermal conditions. Early work in the 1970s by Swaddle and co-workers used hydroxides and oxides as precursors in alkali solutions up to 350 °C.<sup>189</sup> Milder condition are in fact needed when metal salts are used and these can give fine powders directly from solution at 150 °C, or lower.<sup>190</sup> There are many examples of hydrothermal formation of such spinels and some selected examples will be chosen to illustrate the control that can be achieved in synthesis. Rath et al. prepared nanoparticles 9-12 nm in size of Mn<sub>0.65</sub>Zn<sub>0.35</sub>Fe<sub>2</sub>O<sub>4</sub> from chloride precursors in ammonia solution at 180 °C: pH above 10 was optimum and the precipitation of an iron hydroxide before reaction with the other metal salts was found to be necessary to isolate the quaternary oxide.<sup>191</sup> The work was extended to other compositions  $Mn_{1-x}Zn_xFe_2O_4$  ( $0 \le x \le 1$ ), and the nano-sized materials were found to have a different distribution of cations over tetrahedral and octahedral sites than after annealing, as evidenced by irreversible changes in magnetic response after heating above 300 °C;<sup>192</sup> this illustrates how the hydrothermal synthesis can allow access to metastable polymorphs of materials, not accessible by high temperature synthesis. Xia *et al.* prepared similar materials from nitrate salts in NaOH solution and found that only with higher Zn content could Fe<sub>2</sub>O<sub>3</sub> impurities be avoided,<sup>193</sup> while Nalbandian *et al.* used careful pH control to prepare homogeneous nanocrystalline powders, Fig. 8, that had low sintering temperatures to allow the formation of dense, fine-grained microstructures for practical application.<sup>194</sup> Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> can also be prepared at a low temperature of 120 °C.<sup>195</sup>

Nanorods of  $MnFe_2O_4$  were prepared using pre-made nanorods of  $Mn_2O_3$ , demonstrating how the form of solid-state precursors might be used to direct the formation of desired morphology of multi-metal oxide *via* hydrothermal chemistry.<sup>196</sup> It should be noted that  $MnFe_2O_4$  could also be prepared as nanorods directly from metal chlorides treated hydrothermally in sodium hydroxides solution,<sup>197</sup> suggesting that further work is needed to understand crystal growth mechanism.

The use of microwave heating for the hydrothermal synthesis of the spinels  $Co_{1-x}Zn_xFe_2O_4$  and  $Ni_{1-x}Zn_xFe_2O_4$  (x = 0, 0.3, 0.5, 0.7, 1) was shown to be an effective way to give 10 nm diameter crystallites in reactions as short as 10 minutes.<sup>64</sup>

Nanocrystalline  $Cu_{1-x}Co_xFe_2O_4$  ( $0 \le x \le 1$ ) samples were prepared hydrothermally, aided by the surfactant cetyltrimethylammonium bromide (CTAB), and studied for catalysis of the nitration of toluene: the materials with equal amounts of Cu and Co were most active and allowed the regioselective formation of 1,4-dinitrotoluene.<sup>198</sup>

Tiano *et al.* developed a general hydrothermal approach to  $MFe_2O_4$  for M = Mg, Fe, Co, Ni, Cu, and Zn, from simple metal salt precursors in NaOH solution from which crystallite size and shape could be controlled by addition of surfactants.<sup>199</sup> This allowed access to materials with crystallite sizes of just a



**Fig. 8** (a) Bright field TEM micrograph, (b) selected area diffraction and (c) HRTEM image of hydrothermally prepared nanocrystalline  $Mn_{0.8}Zn_{0.2}Fe_2O_4$ . Reprinted with permission from Nalbandian *et al.*<sup>194</sup>

few nanometres up to 10s of nanometres, and a comprehensive set of characterisation measurements allowed structure/ property relationships to be established: this included application as magnetically-recoverable photocatalysts and as mimics of the enzymatic activity of peroxidases, where enhanced activity over pure iron oxides was proven. MFe<sub>2</sub>O<sub>4</sub> with M = Co, Ni, Cu, Zn were also studied as magneticallyseparable catalysts, for epoxide ring opening reactions, and hydrothermally-prepared nanoparticulate CeFe<sub>2</sub>O<sub>4</sub> was found to be the active catalyst.<sup>200</sup>

Aside from magnetic and catalysis properties, other applications of hydrothermally prepared ferrite spinels include NiFe<sub>2</sub>O<sub>4</sub> for the detection of liquefied petroleum gas in air,<sup>201</sup> magneto-dielectric properties of Ni<sub>0.54</sub>Zn<sub>0.48</sub>Fe<sub>1.98</sub>O<sub>4</sub>,<sup>202</sup> microwave absorbing materials  $Co_x(Cu_{0.5}Zn_{0.5})_{1-x}Fe_2O_4$ ,<sup>203</sup> and the absorption of dye molecules for depollution.<sup>204</sup> The spinel  $\beta$ -LiFe<sub>5</sub>O<sub>8</sub> was prepared as a nanocrystalline powder at 140 °C from FeCl<sub>3</sub>·6H<sub>2</sub>O, in equimolar amounts of LiOH·H<sub>2</sub>O and NaOH at 140 °C and their electrochemical capacity was found to be superior to other lithium ferrites.<sup>205</sup>

Diodati *et al.* explored a very easy, low-temperature (T = 135 °C), route based on the coprecipitation of metal precursors from an aqueous suspension containing oxalates combined with a low-temperature hydrothermal treatment.<sup>54,127</sup>

As outlined in the above section concerning green chemistry, time-resolved experiments showed that the formation of crystalline ferrites could be achieved after only 1 to 3 hours of hydrothermal processing,<sup>126</sup> thus disclosing the possibility to implement an energy effective route to the up-scaling of these materials.

This route was further also implemented for the synthesis of quaternary spinel ferrites containing both zinc and either nickel  $(Ni_xZn_{1-x}Fe_2O_4)$  or cobalt  $(Co_xZn_{1-x}Fe_2O_4)$ .<sup>59</sup>

#### Precursors/additives in solvothermal spinel synthesis

Further versatility can be brought to solvothermal synthesis by inclusion of dissolved species, such as salts, surfactants and co-solvents and, in this section, we will consider their benefits for the formation of spinel ferrites. The use of solution additives in solvothermal reactions provides a means to adjust crystal size and shape in the resultant product. Polyethylene glycols, available in a range of molecular weights, are convenient water-compatible solution additives that have been widely studied to control the hydrothermal crystallisation of ferrite spinels: this includes the synthesis of nanocrystalline forms of CoFe<sub>2</sub>O<sub>4</sub>,<sup>84,206</sup> Zn<sub>x</sub>Ni<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub>,<sup>207</sup> Co<sub>x</sub>Zn<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub>,<sup>208</sup>  $Mn_{0.2}Ni_{0.8}Fe_{2}O_{4}, {}^{209}Ni_{0.5}Zn_{0.5}Fe_{1.5}Cr_{0.5}O_{4}, {}^{210}MnxCo_{1-x}Fe_{2}O_{4}, {}^{211}$  $MnFe_2O_4$ ,<sup>212</sup>  $CoCr_xFe_{2-x}O_4$ <sup>213</sup>  $Mn_xNi_{1-x}Fe_2O_4$ <sup>214</sup> and NiFe<sub>2</sub>O<sub>4</sub>.<sup>215</sup> The synthesis of magnetic nickel spinel ferrite NiFe<sub>2</sub>O<sub>4</sub> nanospheres by a reverse emulsion-assisted hydrothermal process proved possible, using ethyltrimethylammonium bromide, polyoxyethylene(10)nonylphenyl ether, iso-amyl alcohol and hexane, in an aqueous medium at 120 °C.<sup>216</sup> This lead to the formation of nanorods of oxyhydroxides and layered hydroxides at short reaction times, prior to the formation of nanospheres of the ferrite spinel.

The use of oleate complexes as reagents in solvothermal ferrite preparation has been studied and the role of the oleate can be as a surface capping agent on the resulting crystallites so to control the crystallite size and shape. A set of the ferrites  $MFe_2O_4$  (M = Co, Ni, Mn, Zn) were prepared from mixed-metal (M,Fe)-oleate complexes upon solvothermal treatment in heptane at 140-180 °C: this yielded 5-6 nm crystallites coated with oleic acid.<sup>217</sup> For CoFe<sub>2</sub>O<sub>4</sub> the choice of solvent mixture and temperature could be used to tune the crystallite size between 5 and 12 mn.<sup>218</sup> In the case of NiFe<sub>2</sub>O<sub>4</sub>, various alcohols and urea were investigated as solution additives to control the crystallite size and shape.<sup>219</sup> Repko et al. prepared a precursor solution of  $Fe(oleate)_3$  and  $Co(oleate)_2$  and used this as a reagent for the solvothermal formation of nanoparticles of CoFe<sub>2</sub>O<sub>4</sub> in water–pentanol mixtures at 180 °C, or in pentanol and 1-octanol (or toluene) at 220 °C.220 The particles could subsequently be surface modified with citrate, or with TiO<sub>2</sub>, via hydrolysis of titanium isopropoxide leading to different dispersions and separations of the nanocrystals, Fig. 9.

Angotzi *et al.* have recently extended the solvothermal oleate route to prepare nanoscale heterostructures that consist of  $CoFe_2O_4$  and  $MnFe_2O_4$  cores with shells of either spinel iron oxide (maghemite/magnetite) or manganese ferrite, added in a second solvothermal reaction, Fig. 10.<sup>221</sup> These complex structures contain an intimate intergrowth between hard (cobalt ferrite) and soft magnetic materials with a hydrophobic coating, and provide a possible means to tune magnetic properties for practical applications.

Acetylacetonates provide convenient precursors for solvothermal synthesis that are soluble in organic solvents. Fe



Fig. 9 CoFe<sub>2</sub>O<sub>4</sub> crystallites of three different sizes (A, B and C) coated with oleic acid, citric acid and TiO<sub>2</sub>. Reproduced with permission from Repko *et al.*<sup>220</sup>

(acac)<sub>3</sub> and M(acac)<sub>2</sub> (M = Ni, Co, Mn, Mg, Zn) treated in water in aloe-vera extract at 200 °C for 2 hours gave agglomerated nanocrystals ranging from 8–45 nm in diameter, depending on the divalent metal.<sup>222</sup> Fe(acac)<sub>3</sub> has also been used as a precursor to other ferrites under solvothermal conditions, including manganese ferrites in oleylamine and phenyl ether.<sup>223</sup> and gallium ferrites using 1,4-butanediol as solvent.<sup>224</sup> Mn<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> nanoparticles were prepared in various polyols from trivalent manganese and iron acetylacetonates directly from solution at 200 °C: this lead to organic coated particles that were soluble in water.<sup>225</sup>

Jolley *et al.* produced Mn–Fe spinels in hydrothermal reactions in the presence of proteins and found protein-encapsulated Mn-ferrites showed different crystal chemistry compared to the pristine materials: in the absence of proteins a solidsolution between  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) and Mn<sub>3</sub>O<sub>4</sub> (hausmannite) was found, but within proteins the Mn end-member was a chalcophanite-like layered Mn oxide.<sup>226</sup>

Heterometallic cluster species provide versatile precursors to mixed-metal oxides since the ratio of metals in the precursors can be pre-defined and intimately mixed prior to the crystal growth of the mixed oxide product. The trinuclear heterometallic acetate clusters [MFe<sub>2</sub>O(CH<sub>3</sub>CO<sub>2</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]·nH<sub>2</sub>O 120 °C (M = Ni, Co, Mn, and Zn) provide a good example and these can be hydrothermally decomposed at 120 °C in water, or various alcohols to yield uniform spinel ferrite nanoparticles.<sup>227</sup> Monodispersed iron cobalt oxide (Fe<sub>2</sub>CoO<sub>4</sub>) and iron manganese oxide (Mn<sub>0.43</sub>Fe<sub>2.57</sub>O<sub>4</sub>) nanoparticles were prepared using bimetallic pivalate clusters of [Fe2CoO- $(O_2CtBu)_6(HO_2CtBu)_3], [CO_4Fe_2O_2(O_2CtBu)_{10}(MeCN)_2],$ and [Fe<sub>2</sub>MnO(O<sub>2</sub>CtBu)<sub>6</sub>(HO<sub>2</sub>CtBu)<sub>3</sub>] using a mixture of oleylamine and oleic acid with either diphenyl ether or benzyl ether as solvent at their respective boiling points of 260 and 300 °C.<sup>228</sup> A similar approach was adopted for the synthesis of ZnFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> from appropriate heterometallic pivalates.<sup>229</sup>

The use of non-aqueous solvents provides a way of modifying crystal growth conditions, by adjusting the solubility of reagents, adjusting diffusion, as well as modifying the pressure at a given temperature. The solvent itself may be reactive, for example, providing reducing or oxidising conditions. Deng et al. pioneered the synthesis of MnFe<sub>2</sub>O<sub>4</sub> ferrites in nonaqueous solvothermal reactions, reporting the formation of monodisperse microspheres for M = Co, Mn, Zn from ethylene glycol with addition of sodium acetate and polyethylene glycol.<sup>230</sup> The sodium acetate was proposed to provide electrostatic stabilisation, while the polyethylene glycol acted as a surfactant to further prevent particle agglomeration. Ethylene glycol as solvent with PEG additive allows access to some intricate and hierarchical crystal morphologies: for example, 100 nm spherical mesocrystals of Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> constructed from agglomerates of primary nanocrystals.<sup>231</sup> Wang et al. prepared hollow CoFe<sub>2</sub>O<sub>4</sub> nanospheres using ethylene glycol as solvent and with urea as an additive, Fig. 11, and the materials were shown to have favourable properties an anodes for lithium-ion batteries.<sup>232</sup>

Otero-Lorenzo *et al.* recently described a comprehensive investigation of colloidal nanocrystal clusters of  $Fe_3O_4$  and  $Mn_xFe_{3-x}O_4$  formed in ethylene glycol using polyethylene glycol and sodium acetate as solution additives.<sup>233</sup> This led to the conclusion that the spinel oxides formed *via* a series of poorly crystalline intermediates followed by the assembly of nanocrystals of spinels into the final colloidal clusters.

#### Continuous routes to ferrite spinels

One advantage of solvothermal routes to oxide materials is the possibility of development of continuous flow methods where solutions of reagents can be pumped through heated pipework that at controlled mixing points gives an industrially-viable production method for the production of nanomaterials at scale.<sup>234,235</sup> In the case of ferrites, this approach has been adopted for several compositions. Cabañas and Poliakoff used



**Fig. 10** Energy-dispersive X-ray maps of metal cation concentration in core-shell nanocrystals of cobalt ferrite and manganese ferrite coated with a second spinel oxide, with line-scans below each map. Reproduced with permission from Angotzi *et al.*<sup>221</sup>



**Fig. 11** Scanning electron microscopy images of CoFe<sub>2</sub>O<sub>4</sub> nanospheres prepare *via* hydrothermal synthesis in the presence of ethylene glycol at reaction times of (a) 6 hours, (b) and (d) 12 hours and (c) 24 hours. Reproduced with permission from Wang *et al.*<sup>232</sup>

a continuous hydrothermal reactor to produce various spinel ferrites including Fe<sub>3</sub>O<sub>4</sub>, MFe<sub>2</sub>O<sub>4</sub> (M = Co, Ni, Zn) and Ni<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> from mixtures of Fe(II) acetate and M(II) acetates.<sup>236</sup> Electron microscopy TEM showed a bimodal particle size distribution with small particles of ~10 nm and larger particles up to 100 nm, and possible reaction mechanisms were discussed, to account for the solution redox chemistry. MeFe<sub>2</sub>O<sub>4</sub> (M = Ni, Cu, Zn) and their solid solution with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> were prepared in continuous flow at 400 °C, 30 MPa with a particle size that increased with increasing residence time.<sup>237</sup> The particles were proposed to form via rapid formation of lowcrystallinity y-Fe<sub>2</sub>O<sub>3</sub> followed by secondary nucleation of the solid solution on its surface with surface dissolution of the primary particles. Stingaciu et al. compared CoFe<sub>2</sub>O<sub>4</sub> samples prepared in a continuous flow reactor with those made in batch reactors and a custom-made spiral reactor; the material made in continuous flow had the narrowest particle size distribution, while magnetic measurements showed a strong interparticle interaction.<sup>238</sup>  $Co_{1-x}Ni_xFe_2O_4$  (x = 0–0.8) nanoparticles were prepared from nitrate precursors in sodium hydroxide solution at 390 °C and 30 MPa: this gave 12-20 nm crystallite with high surface areas and their catalytic properties for CO oxidation and the oxygen evolution reaction were studied.<sup>239</sup>

Recently, some of us have used a continuous hydrothermal flow synthesis (CHFS) approach<sup>59</sup> to prepare crystalline spinel quaternary ferrites  $M_x Zn_{1-x} Fe_2 O_4$  (M = Co, Ni; x = 0.2, 0.35, 0.5, 0.65, 0.8). In particular, the same materials were synthesised both through conventional batch hydrothermal synthesis (HT - as described above) at 135 °C as well as via CHFS. The as prepared compounds were thoroughly characterised from a compositional (ICP-MS, XPS) and structural (XRD) point of view in order to compare the two synthetic approaches and achieve a detailed understanding of how the chosen approach influences the characteristics of the resulting spinel. It could be concluded that CHFS requires higher temperatures and a more complex setup, but is capable of continuous synthesis, and thus can afford a greater quantity of materials over time. In contrast, the simpler HT synthesis was far easier and less time consuming to implement, despite, as a batch method, only being able to yield a limited mass of products in a given time span. Interesting differences were pointed out as far as material composition was concerned: analyses via ICP-MS evidenced that the HT protocol was more successful in affording a good stoichiometric control over the final product by simple adjustment of the nominal stoichiometric ratios between the metal precursors.

#### Hydro/solvothermal approaches to other ferrites

Hexagonal barium hexaferrite,  $BaFe_{12}O_{19}$ , is a material well studied as a hard ferrite used in magnetic recording devices, and hydrothermal routes to the material have been reported, where the aim has been to produce fine powders that can be sintered into magnetic solids.<sup>240–244</sup> Liu *et al.* developed a synthesis route from Fe<sup>2+</sup> and Fe<sup>3+</sup> precursors, with the former being oxidised *in situ* but yielding samples free of Fe<sub>2</sub>O<sub>3</sub> and BaFe<sub>2</sub>O<sub>4</sub> impurities.<sup>245</sup> Related hexagonal ferrites have been

reported via hydrothermal routes including SrFe<sub>12</sub>O<sub>19</sub>,<sup>246</sup>  $Sr_{1-x}Nd_xFe_{12}O_{19}^{247}$  and  $Sr_{1-x}Sm_xFe_{12}O_{19}^{248}$  It should be noted that many of the reported hydrothermal routes to the hexaferrite family involve a second step of calcination to induce crystallinity and to optimise magnetic properties, and hence these are best thought of as processing rather than synthesis routes. For example, although BaFe<sub>12</sub>O<sub>19</sub> forms from solution at sufficiently high hydroxide ion concentration, annealing at 1000 °C is needed to improve saturation magnetisation and intrinsic coercivity.<sup>239</sup> Recent work has examined how the particle morphology of the hexaferrites may be controlled by hydrothermal synthesis: for example, Jing et al. produced M-type SrFe<sub>12</sub>O<sub>19</sub> directly at 220 °C as flake-like particles with magnetic behaviour that depended on grain size.<sup>249</sup> Soria et al. studied SrFe<sub>12</sub>O<sub>19</sub> plates formed by a similar method using a comprehensive set of characterisation methods and found a greater proportion of tetrahedral iron than in reference bulk materials.<sup>250</sup> Dong et al. found a large magnetocrystalline anisotropy in SrFe12O19 nanosheets and measured favourable microwave absorbing properties.<sup>251</sup>

Other multinary iron oxides that have been prepared hydrothermally include the garnet phase  $Sm_3Fe_5O_{12}$ <sup>252</sup> and the sillenite-structured  $Bi_{12}Fe_{0.63}O_{18.945}$  (close to the ideal composition  $Bi_{25}FeO_{40}$ ) and  $Bi_2Fe_4O_9$ .<sup>145</sup>

### Sonochemistry

A relatively little-known approach, which has nevertheless gained significantly more interest in the last five years, is the sonochemical approach. Sonochemistry is based on the formation, growth and collapse of bubbles in a liquid medium (cavitation) by exposure of the system to ultrasonic waves.<sup>2,253–255</sup> Within this context, the act of the bubbles collapsing can cause significant, as well as extremely localised, temperature increases (to around 4750 °C) with equally swift cooling (in excess of 10<sup>10</sup> °C s<sup>-1</sup>)<sup>253</sup> This can be taken advantage of in several ways: it can be used for instance to instantaneously decompose volatile metallorganic compounds to obtain individual metal atoms, agglomerate them and obtain nanoparticles.<sup>253</sup> In other cases (such as many of those examined herein) the localised high temperatures can be used to effectively locally calcine a synthesised material to yield crystalline products without actually needing to bring the entire system to high temperatures;<sup>258</sup> this locally confined calcination" provides the additional benefit that, as an extremely localised phenomenon, it does not give rise to agglomeration or coalescence phenomena in the system (unlike more conventional calcination approaches).<sup>258</sup> Interested readers are referred to more specific works on the approach, such as those by Thompson and Doraiswamy<sup>254</sup> or Mason and Lorimal.<sup>255</sup>

Despite requiring dedicated equipment to suitably generate the cavitation effects necessary for the reactions to take place,<sup>259</sup> the sonochemical approach is, perhaps surprisingly, eminently scalable, able to be employed from the laboratory scale (where a simple ultrasonic rig apparatus may be

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sufficient)<sup>260</sup> to high scale flow reactors;<sup>259</sup> The technical and engineering aspects of this issue have been the subject of a work by Gogate *et al.*<sup>261</sup>

In general, the reports available in the literature on sonochemistry mainly cover spinel ferrites, with the cobalt, zinc and nickel spinels being the most common. Some reports exist concerning perovskite ferrites (namely BiFeO<sub>3</sub>), but in those cases a conventional calcination step was always involved to achieve crystalline materials.<sup>262,263</sup>

Concerning successful and actually low-temperature syntheses, Abbas *et al.*<sup>256,264</sup> were not only able to achieve the synthesis of shape-controlled cobalt spinel ferrite (obtaining both nanocubes and nanospheres – Fig. 12), but also expanded the scope of their research to quaternary ferrites, achieving a mixed Ni/Zn spinel ferrite with controlled stoichiometry. Both these syntheses were carried out at room temperature in deionised water: the metal precursors (chlorides) were dissolved in the aqueous medium and sonicated (Vibra Cell-VCF 1500, Sonics and Materials; 5 cm<sup>2</sup> titanium horn; 20 kHz), before adding 3 M NaOH.

The effect of the confined calcination mentioned above was the subject of a study by Choudhury *et al.*<sup>258</sup> whereby the chemical intermediate reactions for the formation of  $ZnFe_2O_4$ from acetate precursors were hypothesised and compared to the obtained experimental results. Reactions were carried out in a conical flask and an ultrasound bath (capacity: 2.5 L, frequency: 35 kHz, Power: 35 W) was employed for sonication, generating a 1.5 bar ultrasound wave. The study concluded that transient cavitation in the reaction medium provides the energy to promote the *in situ* calcination of oxide particles to yield the ferrite product, with the added benefit of generating smaller size of ferrite crystals compared to conventional calcination. An earlier study by Reddy *et al.*<sup>265</sup> took a more theoretical approach, by coupling experimental results of  $ZnFe_2O_4$  sonochemical synthesis with simulations of the radial motion of cavitation bubbles. In particular, they concluded that the resulting particle size was mainly governed by the rate of production of OH' radicals.

In a more recent work,<sup>257</sup> Chen *et al.* employed sonochemistry to prepare  $ZnFe_2O_4$  nanocubes embellished with reduced graphene oxide for use in electrochemical sensing of biomarkers (specifically 4-nitroquinoline-*N*-oxide) (Fig. 13). Syntheses were carried out at room temperature in deionised water by reacting the nitrate metal precursors with ammonium hydroxide (final pH 8.0) in a 100 W, 40 kHz ultrasonic bath. The graphene oxide was then added by drop-casting.

In work by Harzali *et al.*,<sup>266</sup> the synthesis of the quinary  $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$  spinel through a combination of coprecipitation and ultrasound irradiation was described (Fig. 14). The compound was prepared from sulfate metal precursors in





Fig. 12  $CoFe_2O_4$  nanospheres (a and b) and nanocubes (c and d) synthesised in water through controlled sonochemistry at room temperature. Reproduced with permission from Abbas *et al.*<sup>256</sup>

Fig. 13 Reaction scheme for formation of  $ZnFe_2O_4$ /graphene oxide nanocomposite using sonochemistry. Reproduced with permission from Chen *et al.*<sup>257</sup>



**Fig. 14** TEM micrographs and size histogram of Ni<sub>0.4</sub>Cu<sub>0.2</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> synthesised at T = 90 °C, t = 2 h and for  $P_{diss} = 46.27$  W (1, 2, and 3 represent different areas of the sample; 4 the size histogram). Reproduced with permission from Harzali *et al.*<sup>266</sup>

deionised water by adjusting the pH to 12 with NaOH and sonicating at 28.03, 38.23 or 46.27 W (equivalent to bulk reaction temperatures of 70, 90 and 100  $^{\circ}$ C, respectively). The resulting powders were crystalline after drying and required no further high temperature annealing steps.

Yadav *et al.*<sup>267</sup> were able to prepare  $CoFe_{2-x}Gd_xO_4$  with controlled gadolinium doping levels (x = 0.00, 0.05, 0.10, 0.15 and 0.20). The synthesis was carried out in deionised water at room temperature and the nitrate precursors were sonicated at 20 kHz, 70 W after basification with NaOH. It was shown that doped materials with controlled stoichiometry were afforded by the protocol and the influence of Gd content on structural, magnetic, dielectric, electrical, impedance and modulus spectroscopic features was investigated. The obtained spinels showed potential for applications in microwave and magnetic recording devices and, perhaps more importantly, the method was found to be promising for future synthesis research in the field of rare earth-doped spinel ferrites. Furthermore, the economic and environmental advantages featured by the method make it attractive for possible scaling-up at the industrial level.

Other notable works on the subject include those by Senapati *et al.* (CoFe<sub>2</sub>O<sub>4</sub>),<sup>268</sup> Shafi *et al.* (crystalline CoFe<sub>2</sub>O<sub>4</sub> and amorphous NiFe<sub>2</sub>O<sub>4</sub>)<sup>269,270</sup> and Wu *et al.* (Fe<sub>3</sub>O<sub>4</sub>).<sup>271</sup>

# Microemulsion and miniemulsion synthesis

A very convenient, albeit not easily implemented at the industrial scale, approach to pursue the crystallisation of nanoscale inorganic materials, with a certain control on size, size distribution and shape, relies on carrying out a reaction within the confined environment of micro- and miniemulsion droplets, which act as "nanoreactors".<sup>272</sup> This class of methods, typically based on the precipitation of the targeted oxide within the confined space of water droplets dispersed in a continuous apolar phase, as described extensively in the following, cannot be classified as fully "green" methods because of the use of organic solvents such as cyclohexane. Nevertheless, they present unique features, such as the exploration of unconventional crystallisation pathways<sup>272</sup> and the possibility to pursue the crystallisation of the targeted oxides already at room temperature.<sup>273-275</sup> Indeed, also in this case, as in the above described solvo- and hydrothermal routes, formation of phases which would not be affordable by high temperature routes. Micro- and miniemulsions differ not only because of their different typical droplet size, but also regarding their thermodynamics viz. kinetic stability. Microemulsions<sup>276</sup> are thermodynamically stable colloidal dispersions, characterised by droplets with an average hydrodynamic diameter of 5-50 nm, that are spontaneously formed by mechanical stirring,277,278 whereas miniemulsions<sup>279-282</sup> are kinetically stable systems, consisting of droplets with an average size of 30-300 nm, generated by using high shear forces.<sup>279-282</sup> Since the synthesis of oxides is typically performed through precipitation reactions in a water medium, the formation of oxides within droplets is

generally carried out in inverse (water-in-oil) emulsions (also referred to as "reverse micelles"), by mixing an emulsion containing an aqueous metal salt precursor solution with a second one containing a precipitating agent (acid/base). Whereas, in the case of microemulsions, the droplet collisions result in the fusion and mixing of the reactants, with slower characteristic exchange times compared to the diffusion of reactants in bulk conditions,<sup>283</sup> miniemulsion droplets can instead be considered as independent nanoreactors, in which reactions run in parallel. Miniemulsion droplets are stable against diffusional degradation processes and collisions are hindered. As a consequence, in order to promote the collision and fusion of the droplets and consequently the mixing of the reactants, ultrasounds, providing the high shear forces needed for disrupting the droplets, are necessary.<sup>284</sup> For the synthesis of ferrites, microemulsions have been broadly used, whereas only few examples concerning the use of miniemulsion to achieve ferrites have been reported. In the following section, the state-of-the-art in the micro- and miniemulsion synthesis of ferrites is summarised. It is worth highlighting that, in many cases, oxo/hydroxo metal compounds were achieved as a first product of microemulsion synthesis, which in turn needed a further thermal treatment to be converted into crystalline ferrites. Most of these examples, have deliberately not been reported in this contribution, as it is focussed on low temperature routes to ferrites.

# Microemulsion and miniemulsion routes to perovskite and spinel ferrites

A very comprehensive review on the use of microemulsion for the synthesis of ferrites was authored by Mathew,<sup>34</sup> summarising different protocol examples, typically relying on water-inoil emulsions, based on a CTAB/1-hexanol/water system. In these routes CTAB acts as the surfactant. Different examples of the microemulsion-based synthesis of various spinel ferrites, such as zinc ferrite, nickel–zinc ferrite, manganese–zinc ferrite and cobalt ferrite, are provided. In some cases, different oil/ surfactants formulations were used, as exemplified in Fig. 15.

Very recently, Scano *et al.*<sup>285</sup> have also published a comprehensive review on the preparation of ferrites by microemulsions, presenting a series of advantages with respect to other methods, due to the possibility of confining reactions in nanosized reactors, allowing the preparation in mild synthesis conditions of a wide variety of nanostructured ferrites with controlled composition, particle size and shape.

In a more general work,<sup>286,287</sup> the potential of reverse micelles as nanosized aqueous droplets, existing at certain compositions of water-in-oil microemulsions, is presented for the controlled synthesis of nanoparticles, among which also ferrites. The review firstly presents to the reader the basic concepts in the field of reverse micellar synthesis of materials; then the typical synthesis pathways and the correlations between the properties of the microemulsion reaction media (*e.g.* reagent concentrations, ionic strength, temperature, aging time) and the prepared materials are presented.



**Fig. 15** Flow chart of the typical experimental procedure for the micromulsion synthesis of ferrite nanoparticles (adapted with permission from Mathew *et al.*).<sup>34</sup> SDS: sodium dodecyl sulphate.

A further pivotal report in this regard is the work by Aubery et al.,<sup>288</sup> which thoroughly discusses the phase behaviour, dynamics, and structure of water-in-oil (w/o) microemulsions of the aqueous solution/1-hexanol/isooctane system with the goal of determining their effect on Mn-Zn ferrite nanoparticle formation, kinetics and characteristics. The same authors,<sup>289</sup> carried out a further fundamental systematic study devoted to investigate the formation of w/o microemulsions with high aqueous phase uptake in a non-ionic surfactant system as a reaction medium for the synthesis of Mn-Zn ferrite nanoparticles. In particular, a comprehensive study, based on the phase behaviour of systems containing precursor salts and the precipitating agent, was carried out to correlate the phase diagrams with the internal structure and dynamics of microemulsions, which in turn could be related to the final features of the resulting Mn-Zn spinel and superparamagnetic ferrites. This study must be considered relevant in this context, since it sets the knowledge base for a deeper understanding of the relationship between the final characteristics of the obtained materials with the properties of the reaction medium, *i.e.* the microemulsion.

The unusual conditions achieved by using microemulsions as reaction media was the topic of a further investigation by Bellusci *et al.*<sup>290</sup> The authors, through a comprehensive approach, pointed out that the physico-chemical equilibria that influence the precipitation of spinel manganese ferrites from an aqueous solution can be substantially altered when the process is carried out in a microemulsion system consisting of a toluene/water/sodium dodecylbenzenesulfonate system. However, prior to the unavoidable final calcination step, only the presence of nanosized mixed hydroxide com-

pounds could be ascertained, a result which was ascribed to a low metal content and a limited matter exchange among aqueous nanodroplets, likely inhibiting the hydroxide to oxide transformation inside the selected micellar system.

In a further work,<sup>291</sup> MgFe<sub>2</sub>O<sub>4</sub> was obtained using a tertiary heptane/Igepal CO 520/H<sub>2</sub>O, system and the effect of the water-to-surfactant ratio on particle size and magnetic properties was studied, whereas a similar investigation by the same authors<sup>292</sup> focussed on the effects which changing the continuous phase had on the particle size and the magnetic properties of the resulting Mg spinel. The same compound was addressed by Holec *et al.*<sup>293</sup>

The effect of the experimental parameters on the final features of the resulting ferrites was also the topic of a thorough investigation by Pemartin et al.<sup>66</sup> An oil-in-water (o/w) microemulsion was used for the preparation of Mn-Zn ferrite magnetic nanoparticles (NPs). By variating the precipitating agent and the oil phase concentration, Mn-Zn ferrite nanoparticles with different characteristics could be obtained and it could be shown that, at a fixed microemulsion composition (surfactant: water weight ratio (S:W) 25:75, 12 wt% oil phase), the use of NaOH as precipitating agent resulted in smaller nanoparticles compared to when tetramethylammonium hydroxide was used (2.4 nm vs 5.2 nm, respectively). Additionally, particle size was shown to increase with higher oil content (9.4 nm for 20 wt% oil), a result which was ascribed to the higher concentration of precursor in the microemulsion. In conclusion, crystallite size varied depending on microemulsion composition and precipitating agent; consequently the magnetic characteristics (blocking temperature and saturation magnetization) also changed as a function of the precipitating agent and microemulsion composition.

Different spinel ferrites, ranging from  $\text{CoFe}_2\text{O}_4$ ,<sup>294–296</sup> to Ni and Zn ferrites,<sup>297,298</sup> to  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ,<sup>299</sup> to  $\text{Mn}^{3+}$  substituted  $\text{MnFe}_{2-x}\text{Mn}_x\text{O}_4$  ferrite,<sup>300</sup> to  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  (x = 1, 0.8, 0.6, 0.5, 0.4, 0.2, 0.0),<sup>301,302</sup> to  $\text{Co}_{0.3}\text{Cd}_{0.7}\text{Zn}_{1.5x}\text{Fe}_{2-x}\text{O}_4$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5),<sup>303</sup> to  $\text{Ni}_x\text{Co}_{(1-x)}\text{Fe}_2\text{O}_4$  (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0),<sup>304</sup> to  $\text{CoCrFeO}_4$ ,<sup>305</sup> to  $\text{MFe}_2\text{O}_4$  (M = Co, Fe, Mg, Mn, Cr, Zn) have been prepared by these routes.<sup>306</sup>

By the microemulsion route, doped spinel ferrites could also be easily achieved, as reported by Baig *et al.*<sup>307</sup> for the rare earth  $Dy^{3+}$  substituted MnFe<sub>2</sub>O<sub>4</sub> nanoparticles, though in this case a final heating step at 400 °C in vacuum was needed to achieve a crystalline nanomaterial.

In an interesting example of combining different synthetic routes, Antonello *et al.*,<sup>15</sup> reported the synthesis of several crystalline first-row-transition-metal (Mn, Fe, Co, Ni, Cu, and Zn) ferrites prepared by a combination of miniemulsion synthesis and solvothermal treatment, pursuing unconventional conditions in terms of space confinement, temperature, and pressure. This synergy allowed to obtain the crystalline ferrites at a much lower temperature (*i.e.*, 80 °C) than usually required and without any post-synthesis thermal treatment. X-ray diffraction revealed that analogous ferrites synthesised by miniemulsion at ambient pressure or in bulk (*i.e.*, from an aqueous macroscopic solution and not in the confined space of the miniemulsion droplets) either at ambient pressure or under solvothermal conditions did not result in similarly highly crystalline products. Concerning their functional behaviour, the synthesised ferrites were superparamagnetic and were found to be active oxidation catalysts, as demonstrated for the oxidation of styrene, which was taken as a model reaction. Thanks to their magnetic properties, the catalysts could be recovered from the reaction medium by magnetic separation and reused for several cycles without loss in activity.

A further combination of approaches was presented by Tajik *et al.*,<sup>308</sup> who prepared  $CuFe_2O_4$  nanoparticles with an average particle size of 22.3 nm by a combined microemulsion and homogenous precipitation method.

In a report by Ahmad,<sup>72</sup> the microemulsion synthesis of spinel nanoferrites having a nominal composition of  $Sr_{1-x}Nd_xFe_{2-y}Cd_yO_4$  (0.0  $\leq x \leq$  0.1, 0.0  $\leq y \leq$  1.0) and an average crystallite size in the 23–35 nm range is described. Quaternary ferrites were also prepared by using the microemulsion route. Ali *et al.*<sup>309</sup> prepared nanosized Zr–Co doped nickel ferrites with a nominal composition, of NiZr<sub>x</sub>Co<sub>x</sub>Fe<sub>2-2x</sub>O<sub>4</sub> (x = 0.0, 0.2, 0.4, 0.6, 0.8) by using this method.

# Microemulsion and miniemulsion routes to hexaferrites and further ferrites

Ali<sup>310</sup> reported a series of complex transition metal/rare earthbased Y-type hexaferrites synthesised by the microemulsion method. Interestingly, the microemulsion route allowed controlled doping, and the effect of doping with manganese (at the tetrahedral site) and with terbium (at octahedral site) could be investigated. It was observed that changes occurred in magnetic properties (such as saturation magnetisation, coercivity, remanence and magnetic moment) due to the cationic stoichiometry and their occupancy in the specific sites.

Differences in the structural and magnetic properties of nanosized barium hexaferrite powders, prepared by single and double microemulsion techniques, were the topic of a study by Koutzarova et al.<sup>311,312</sup> In detail, barium hexaferrite powders, featuring nanometric particle sizes, were prepared by either single or double microemulsion (water-in-oil reverse microemulsion system with cetyltrimethylammonium bromide (CTAB) as a cationic surfactant, *n*-butanol as a co-surfactant, n-hexanol as a continuous oil phase, and an aqueous phase) and the influence of the type of microemulsion technique on the microstructure and on the magnetic properties of the barium hexaferrite powders was studied. The type of microemulsion adopted was shown to affect, inter alia, the average particle size, the shape and the functional properties: ferrites obtained by single microemulsion featured better magnetic characteristics than those obtained by double microemulsion. It should be also pointed out that barium ferries had already been prepared by microemulsion by further authors.<sup>313</sup>

Murtaza *et al.*<sup>314</sup> further employed the microemulsion approach to prepare different Nd–Mn-substituted hexaferrites having general formula  $Sr_{2-x}Nd_xNi_{0.5}Co_{1.5}Fe_{12-y}Mn_yO_{22}$  (x = 0.0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, y = 0.0, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75).

# Microwave-assisted synthesis of ferrites

The liquid phase synthesis of nanomaterials using microwaveassisted heating has received considerable attention from the scientific community in the last years because it allows rapid volumetric heating, thus enabling remarkable increase of reaction rate, selectivity and yield compared to conventional approaches. This scenario offers attractive perspectives in the fabrication of materials at low cost, improving energy savings and process efficiency.

Microwaves are electromagnetic radiation with frequencies between 0.3 and 300 GHz and wavelengths ranging from 1 mm to 1 m, positioned between infrared and radio wave in the electromagnetic spectrum. For laboratory and domestic application, the usual frequency for microwave heating is 2.45 GHz, corresponding to a wavelength of 12.24 cm. In general, any material containing mobile electric charges such as polar solvents or electrolytes, can be heated by microwaves. Heat is generated by rotation, friction and collision of polar molecules such as water, which try to orientate towards the oscillating electric field (Fig. 16a). In conventional heating systems the thermal energy needs to be transferred from the heating source to the reactor, to the solvent and ultimately to the reactants, which requires large amount of time and of energy dissipation. In contrast, in microwave-based setups the heating occurs directly at the target system, thus making the use of energy sources and energy transfer media (e.g. oil bath) superfluous and remarkably improving the time and energy savings (Fig. 16b). There is an extensive number of reports in the literature showing that microwave heating largely increases the rate of chemical reactions. In order to explain the rapid temperature increase promoted by the microwave irradiation, the existence of effects called "specific microwave effects" and "nonthermal microwave effects" was postulated.315-317 "Specific microwave effects" consider that the thermal heating effect does not have repercussions on the mechanism of the chemical reaction but only influences the reaction time through the formation of hot spots in the reactor. In contrast, "non-



**Fig. 16** (a) Water molecules in an alternating electrical field under microwave irradiation (from ref. 323) (b) Time-temperature correlation of conventional and MW-heated reaction vessels as well as the temperature distribution inside the reaction mixture. Reproduced with permission from Schütz *et al.*<sup>324</sup>

thermal microwave effects" predict direct interactions between the molecules and the microwaves in the solution reaction. Possible implications may regard the reaction activation energy or excitement of rotational/vibrational molecular transitions.<sup>318–320</sup>

The heating generated by microwave radiation in a solvent or material is determined by the loss tangent  $\tan \delta = \delta''/\delta'$ , where  $\delta''$  is the dielectric loss, *i.e.* the amount of radiation converted into heat, and  $\delta'$  represents the dielectric constant, which gives the polarisability of molecules in the electric field.<sup>315,321</sup> To understand the microwave-matter interaction the penetration depth of the radiation should be also considered. This denotes the depth where the incoming microwave power is reduced to the 37%. The penetration depth is inversely proportional to the loss tangent: it grows with increasing material temperature and decreases by enhancing the radiation frequency.<sup>322</sup> For water, which is one the most used solvent in liquid phase syntheses, due to its large availability and environmental-friendly character, the penetration depth at room temperature conditions is approx. 2 cm. Even though this value doubles at 80 °C its dielectric loss drops remarkably, complicating the microwave heating at high temperatures. However, as water is a polar solvent, is considered also a good microwave absorber. When microwave irradiated, the polarised water molecules tend to orientated following the alternating electric field (Fig. 16a). Heat is consequently produced by the rotation, friction, and collision of the molecules. The amount of time required for the molecules to relax is directly correlated to their volume and the extent of the hydrogen-bonding network. As the relaxation time depends on the loss tangent of the solvent, the denser is hydrogen-bonding network, the higher will be the heat developed by irradiation. When electrolyte solutions are considered, the relaxation time decreases at low salt concentrations and then increases again. This behaviour is explained by the initial rupture of the hydrogen bonding network. Even if some molecules are coordinated to the ions, the majority of them do not experience strong intermolecular forces and possess lower relaxation time. At high salt concentration, greater ordering of the water molecules presumably sets in, thus inducing even larger relaxation times than for pure water.321

Owing to the manifold advantages offered by water in the synthesis of nanostructured materials, numerous scientific publications have dealt with the employment of microwave radiation in combination with wet chemistry processes. In the following sections the main progress on the microwaveassisted synthesis of ferrites with spinel and perovskite structures in aqueous and other solvents will be highlighted.

#### Ferrites with spinel structure

The microwave heating has been combined with diverse wet chemistry procedures for the synthesis of spinel ferrites. These comprise hydrothermal, solvothermal, sol–gel and polyol methods.

Among these routes, the hydrothermal approach was the first procedure to be coupled with such electromagnetic fields.

Komarneni et al.<sup>325</sup> showed more than two decades ago how  $MFe_2O_4$  with M = Mn, Co, Ni, and Zn powders could be obtained from the basic solution of the nitrate salt precursors in few minutes at 164 °C, increasing the reaction kinetics by almost two order of magnitudes with respect to conventional routes. Interestingly, the prepared materials exhibited also high porosity and specific surface areas from 72 to 247 m<sup>2</sup> g<sup>-1</sup>, most probably due to nanoparticle aggregation during the synthesis. A few years later Kim and co-workers<sup>64</sup> implemented the work of Komarneni et al. for the preparation of Co-Zn and Ni-Zn ferrite powders from chloride precursors at 100 °C within 30 min. The incorporation of Zn in the lattice positions of Ni and Co was verified by the lattice parameter increase proportional to the Zn amount. In the past years, the use of additives in the hydrothermal process has become common to control finely the properties of the synthesised materials. The addition of ionic liquids to the water-based reaction mixture and the subsequent microwave heating has had a remarkable influence on the crystal structure of the final products. A transition from ZnFe2O4 and α-Fe2O3 mixed phases, to pure ZnFe<sub>2</sub>O<sub>4</sub> and pure  $\beta$ -FeOOH was observed by increasing amount of ionic liquid.<sup>326</sup> The spinel structures obtained in such way exhibited also encouraging photocatalytic activity for phenol degradation. ZnFe2O4 nanoparticles were employed as catalyst precursor by Choi et al.<sup>327</sup> for the synthesis of hydrocarbons by reducing CO2. The microwave-assisted hydrothermal synthesis produced spinel nanoparticles agglomerates with high surface area (119  $\text{m}^2 \text{g}^{-1}$ ) and improved morphology stability under reduction conditions at 400 °C. Microwave heating offers an unconventional way to prepare materials, which usually require elevated temperatures and prolonged reaction time. This is the case of layered metal oxides as sodium/potassium iron oxide nanosheets,328 prepared by microwave-assisted hydrothermal method at 180 °C within 5 minutes. The layered compounds consist of two-dimensional iron oxide building blocks separated by intercalated alkali ions (Fig. 17). Such nanosheets exhibit ferromagnetic properties due to the magnetic anisotropy of the iron oxide layers. Moreover, the lamellar structure enables high ion diffusion



**Fig. 17** (a) XRD pattern of sodium iron oxide nanosheets synthesised under microwave irradiation at 180 °C for 5 min. (b) Crystal structure of Na<sub>2.4</sub>Fe<sub>10.99</sub>O<sub>16.03</sub> viewed perpendicular to the *c* axis. The pink, red, and grey spheres correspond to Na, O, and Fe atoms, respectively. Reproduced with permission from Wu *et al.*<sup>328</sup>

and thus promising application in high performance lithiumion batteries.

The application of microwave radiation for the hydrothermal synthesis of spinel ferrites resulted also in improving the materials' magnetic properties and their applications as magnetic resonance contrast agents. Thus, Williams and coworkers<sup>329</sup> showed that microwave heating induced the formation of small and highly uniform polyelectrolyte functionalized Fe<sub>3</sub>O<sub>4</sub> particles with much larger magnetic saturation than materials prepared by conventional hydrothermal methods. The application of electromagnetic fields allows therefore greater control over the final functionality of the ferrites for magnetic resonance applications.

One of the first examples in exploiting the benefits of the microwave radiation within solvothermal synthesis was reported by Caillot et al. in 2002 330 for the preparation of magnetite nanoparticles. Using a home-made microwave autoclave the authors succeeded in the preparation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles of 20 nm size within 10 minutes starting from ferrous chloride solution in ethanol. Compared to conventional solvothermal procedures the materials were obtained 10 times faster and with lower grain size. The use of surfactants has been implemented in solvothermal synthesis to enable better control of particle growth and morphology. The introduction of cetyltrimethylammonium bromide in an ethanol solution of iron and zinc metalorganic precursors, lead to the rapid synthesis of ZnFe<sub>2</sub>O<sub>4</sub> at temperature below 100 °C with crystallites ranging between 8 and 20 nm, even if in the final material significant organic contaminations originated from the solvent or surfactant molecules were present.332 Diols and in general polyols are in general preferred to surfactants because their bifunctional character to act both as solvent and capping agent, limits the organic content in the reaction mixture. The 1,2-propandiol-based solvothermal synthesis of CoFe2O4 was employed to generate nanoparticles of average size of about 5 nm.333 Also in this case the materials presented organic surface contamination from the solvent, however they showed interesting magnetic behaviour. With respect to bulk and conventionally prepared systems, ferrites prepared through this microwave-assisted method possessed much larger magnetic saturation at 10 K.

The microwave-assisted synthesis of metal ferrites using other polyols, such ethylene glycol, offered an interesting tool to further control nanoparticle microstructure and morphology. Giri *et al.*<sup>334</sup> were among the first to develop a microwave refluxing approach for the preparation of metal ferrites. The bifunctional role of ethylene glycol as solvent and capping agent led to phase pure  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $0 \le x \le 0.8$ ) nanoparticles within few minutes, the crystallinity of which could be improved by increasing the pH of the starting solution. The group of Kozakova<sup>335</sup> showed later how the combination of ethylene glycol and water could be beneficial for directing the structural properties of ferrite materials. They showed that the addition of small portions of water to ethylene glycol in a microwave-assisted environment, lead to Fe<sub>3</sub>O<sub>4</sub> particle size reduction up to one third of the original size and to the formation of nanoparticles in superparamagnetic and ferromagnetic states.

Further works made use of larger polyols as triethylene glycol  $(TREG)^{331,336-339}$  as solvent. The high stabilising properties of TREG enables high dispersion of the nanoparticles without the need of further additives. Solano *et al.*<sup>338</sup> compared the synthesis of MFe<sub>2</sub>O<sub>4</sub> (M = Fe, Co, Mn, Ni, and Zn) through solvothermal and microwave-assisted routes in TREG. With both methods, particles of similar size were obtained. However, the use of microwave heating, besides shortening the reaction time, significantly influenced nanoparticle nucleation, leading to monodisperse size distribution and absence of nanoparticle aggregation (Fig. 18).

In order to better highlight whether microwaves influence the ferrite synthesis, the same authors performed a structural comparison with the solvothermal synthetic route on the same systems prepared in ref.<sup>338</sup> using X-ray and neutron diffraction methods.<sup>331</sup> With the only exception of ZnFe<sub>2</sub>O<sub>4</sub>, for which the microwave synthesis induced much higher inversion degree than the thermal approach, the cationic distribution microstructure and magnetic properties of the materials were very similar independent of the synthesis method used. In particular, neutron diffraction studies demonstrated the absence of H atoms and related organic matter coming from the TREG capping ligand, pointing out the improved dispersion of microwave-assisted materials. Schneider and co-workers demonstrated how the TREG-based microwave synthesis is also suitable for upscaling magnetite nanoparticles from milligram to grams.<sup>339</sup> Even though the scalability of the nanoparticles increased their size polydispersity, most likely due temperature gradient issues in the reaction vessel, the materials were produced below 1 h and still possessed high saturation of magnetization.

Besides hydrothermal and solvothermal approaches, which represent the majority of the synthesis processes, the microwave heating for the preparation of spinel ferrites has been combined also with combustion<sup>340,341</sup> and sol–gel methods.<sup>342–344</sup>



**Fig. 18** TEM images of MFe<sub>2</sub>O<sub>4</sub> nanoparticles synthesized by the thermal and microwave synthetic routes. For all the investigated cases, the microwave synthesis produces highly homogeneously dispersed nanoparticles. The numbers below each image display the average nanoparticle size with its deviation. Reproduced with permission from Solano *et al.*<sup>331</sup>

Review

The magnetic properties and antimicrobial performance of NiFe<sub>2</sub>O<sub>4</sub> nanopowders prepared with microwave-assisted combustion method were compare to those obtained via conventional approaches.<sup>340</sup> The faster synthesis induced by the electromagnetic fields engendered nanoparticles with almost half of the size of those obtained by standard procedures. As a result, the materials possessed improved magnetic properties and antimicrobial character. In another work, conventional and microwave methods were compared using urea and citric acid fuels for the synthesis of CoFe<sub>2</sub>O<sub>4</sub> nanopowders.<sup>341</sup> The weaker chelating power of urea with respect to citric acid failed to deliver phase pure ferrites for both approaches. Using citric acid, microwave ignition engendered larger sphere-like ferrite particles with higher inversion degree than those obtained with the conventional approach. For these reasons, and despite small impurities of CoO and CoFe, the microwaveassisted materials also showed better magnetic properties.

The combination of microwave heating with non-aqueous sol-gels offers an intriguing chance for the rational design of spinel ferrite materials beyond the simple synthesis of nano-particles. Niederberger and co-workers showed how the reaction of metal acetate or acetylacetonates with benzyl alcohol in presence of microwave irradiation yielded Fe<sub>3</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub>, and NiFe<sub>2</sub>O<sub>4</sub> nanoparticles within 12 minutes at 170 °C.<sup>342</sup> The introduction into the reaction mixture of glass substrates or metal nanoparticles enabled the preparation of ferrite thin films and core–shell systems, respectively (Fig. 19).

This route was implemented by Suchomski *et al.*<sup>343</sup> for the synthesis of monodispersed  $ZnFe_2O_4$  nanoparticles of spherical shape. Detailed structural and magnetic characterization evidenced an inversion degree of 68% and the presence of a superspin glass state with freezing temperature of about 22 K. In addition, the materials exhibited promising performance as anode material for Li-ion battery with little capacity fading after hundreds of cycles.

Furthermore, the coating capability of the microwaveassisted sol-gel approach has been used for the preparation of



**Fig. 19** (a) General reaction scheme displaying the metal oxide precursors employed in the sol-gel synthesis, the solvent, the experimental conditions, and the final composition of the nanoparticles. Photographs of (b) magnetite nanopowder under the influence of a permanent magnet, (c)  $CoFe_2O_4$  dispersion in ethanol, and (d)  $CoFe_2O_4$  film on a glass substrate. Reproduced with permission from Bilecka *et al.*<sup>342</sup>

ordered macroporous magnetic  $MnFe_2O_4$  architectures through nanoparticle deposition on sacrificial colloidal crystals.<sup>344</sup> The control of synthesis parameters such reaction time enabled tuning of the coating thickness and layer homogeneity.

#### Ferrites with perovskite structure

In contrast to the spinel structure, perovskites are characterised by large size difference between the A and B cations. This has strong repercussions on their synthesis conditions, such that perovskite systems tend to require higher temperatures for their formation compared to spinels.<sup>346</sup> Therefore, the low temperature synthesis of ferrites with the perovskite structure is less common. The main contributions in the literature on this field regard mainly BiFeO<sub>3</sub>. In combination with microwave irradiation, the hydrothermal method represents the principal low temperature synthetic approach. To ensure homogeneous cationic intermixing, avoid the formation of multiphase impurities, and control the particle morphology, polyelectrolytes or surfactants are generally employed in the reaction mixture. Chybczynska and co-workers showed how the petal size and crystallinity of BiFeO<sub>3</sub> flower-like particles increased with the amount of polyethylene glycol used in the microwave-assisted hydrothermal synthesis, which was directly correlated with a decrease of the magnetic properties.347 Besides its interesting magnetic properties, BiFeO<sub>3</sub> is a wellknown photocatalyst. With respect to conventional hydrothermal method, the preparation of bismuth ferrite with the assistance of microwave heating resulted in materials with higher crystallinity and specific surface area, ascribed to nonthermal effects of microwave during the synthesis.<sup>348</sup> As a result, the materials possessed better photocatalytic properties for the photodegradation of organic dyes. Similar photocatalytic tests were performed by Huang et al.<sup>349</sup> on BiFeO<sub>3</sub> materials prepared by a microwave-assisted hydrothermal approach using different surfactants molecules as capping agents. The employment of polyvinylpirrolidone instead of EDTA engendered materials with almost four times higher specific surface area, which lead to a significant improvement of the material's photocatalytic performance.

The perovskite structure is well-known for its structural flexibility enabling the incorporation of substitutional metal ions. However, there are very few examples of doped perovskite ferrites in literature obtained by low temperature approaches with the assistance of electromagnetic heating. Ultrathin (~2.5 nm) Cr-doped BiFeO<sub>3</sub> ferroelectric films were obtained by hydrothermal approach without any use of mineralizer.<sup>350</sup> Due to the microwave-assisted approach, after only 2 cycles irradiation, atomic step terraces were observed on the films indicating the high ordered growth of the film. The resistive switching behaviour of the films was confirmed by electrical characterization and thermoionic emission was demonstrated to be the dominating charge transport behaviour. Ponzoni et al.155 showed how the preparation of A-site substituted  $Bi_{1-x}La_xFeO_3$  up to x = 0.45 could be remarkably accelerated using microwave-assisted hydrothermal synthesis with respect



**Fig. 20** SEM images of  $SrTi_{1-x}Fe_xO_3$  samples prepared *via* microwaveassisted hydrothermal method: x = 0.0 (a), 0.05 (b), 0.1 (c), 0.25 (d), 0.4 (e); (f) EDX spectrum of the x = 0.25 sample Reproduced with permission from da Silva *et al.*<sup>345</sup>

to the conventional method. In a further, report solid solutions of  $SrFeO_3$  and  $SrTiO_3$  in form of nanocubes could be prepared at 140 °C and a constant pressure of 3 bar by a microwave heated hydrothermal approach (Fig. 20).<sup>345</sup> X-ray and UV spectroscopies revealed that the  $Fe^{2+}/Fe^{3+}$  ions occupy the  $Ti^{4+}$  sites and that the band gap progressively decreases with the iron amount. In the same work, this synthetic route was also used to prepare films by the tape casting or the suspension methodology.

### Other approaches

In this section we will provide examples of synthesis approaches that are not sufficiently featured in the literature to merit their own section. Broadly, they belong to one of two subsets: (i) methods that are not particularly popular (generally because other, more widespread approaches are considered preferable and/or less complex) and (ii) methods that generally involve a high-temperature calcination step and therefore only feature very few examples that may qualify as low-temperature (coprecipitation<sup>353</sup> is one of these latter approaches).

Biosynthesis, includes syntheses where the chemical reactions are aided by biological systems (*e.g.* by having bacteria reduce metal cations through anaerobic respiration).<sup>351</sup> Byrne *et al.*<sup>351</sup> synthesised zinc-substituted magnetite  $Zn_xFe_{3-x}O_4$  (*x*  = 0.00, 0.16, 0.42, 0.56, 0.92) through bacterially-assisted synthesis whereby zinc and iron oxyhydroxides were initially coprecipitated from an aqueous solution and then were inoculated with a culture of *Geobacter sulfurreducens* (0.2 mg mL<sup>-1</sup> protein) and acetate (acting as electron donor for the reduction) and incubated in the dark at 30 °C. Crystalline nanoparticles (Fig. 21) with enhanced magnetic properties were thus obtained.

Similarly Céspedes *et al.*<sup>61</sup> employed bacterial synthesis to prepare several different Zn- or Co-doped ferrite spinel nanoparticles with citric acid coating for applications in magnetic hyperthermia therapy  $M_xFe_{3-x}O_4$  (M = Co, Zn; x = 0.00, 0.16,0.42, 0.71). As described by Byrne *et al.*, Fe and M oxohydroxide mixtures were coprecipitated from an aqueous medium and then treated with a *Geobacter sulfurreducens* culture. It was found that the stoichiometry of M in the final ferrite could be controlled by varying the concentration of M in the M–Fe<sup>III</sup>oxyhydroxide intermediate species.

Whereas ball-milling is a well-known top-down dry synthesis method for ferrites,  $^{354-357}$  Chen *et al.* $^{358,359}$  combined ball-milling and ultrasound technology in an aqueous suspension to obtain nickel and manganese spinel ferrite nanoparticles. In both cases the M precursors (either MnO<sub>2</sub> or NiCO<sub>3</sub>·2Ni(OH)<sub>2</sub>·4H<sub>2</sub>O) were milled at room temperature in 1000 ml of ultrapure water together with the iron precursor (either metallic iron powder or iron coming directly from pure iron milling balls). The diameter of the milling balls was 1.0–1.5 mm and a ball to powder mass ratio was 100:1. The rotation speed of stirrer was 235 rpm, and the ultrasonic intensity and power were 40 kHz and 200 W, respectively.

The sol-gel auto-combustion approach (and the citrate method in particular), is widely known and applied in the field of ferrite synthesis,<sup>360–363</sup> but in most cases either the auto-combustion process must be triggered at high temperatures, or a calcination step is then employed to reach crystallisation. By contrast, Xiao *et al.*<sup>352</sup> achieved the cobalt spinel



**Fig. 21** TEM images showing (a) Zn<sub>0</sub>, (b) Zn<sub>0.16</sub>, (c) Zn<sub>0.42</sub>, (d) Zn<sub>0.56</sub>, (e) Zn<sub>0.92</sub>, and (f) size distributions of all samples prepared through bacterially-assisted synthesis. Data obtained by measurement of n = 200 particle diameters per sample. Reproduced from Byrne *et al.*<sup>351</sup>



**Fig. 22** Cobalt spinel  $CoFe_2O_4$  synthesised by a modified citrate solgel approach: TEM morphology of the as-burnt powder (a) and corresponding grain size histogram obtained by statistical method (b). Reproduced with permission from Gass *et al.*<sup>352</sup>

 $CoFe_2O_4$  by a modified citrate sol-gel approach, affording auto-combustion and formation of crystalline cobalt ferrite powder already at 200 °C (Fig. 22). The synthesis, from an aqueous mixture of citric acid and metal nitrates was stirred at pH 6 until a sol formed. This sol was changed to a gel at 80 °C and into a xerogel at 120 °C. Finally, auto-combustion was triggered at 200 °C yielding the ferrite powder. The combustion was proven to be a thermally induced anionic redox reaction, with carboxyl group as reductant and nitrate ions as oxidant.

### Conclusions

We have collected and reviewed recent contributions concerning different wet-chemistry routes, having as common factor the use of low temperature, for the synthesis of different classes of ferrites, focussing largely on materials belonging to the spinel, perovskite and hexaferrite families. The discussion of the different examples reported illustrates that this relevant family of functional materials can be also addressed by relatively environmentally friendly and, in many cases, simple to or suspension-based implement solutionsynthesis approaches. As well as complying with the principles of 'green chemistry' the solution-mediated synthetic methods that we have surveyed offer the prospect of industrially-scalable manufacture of materials, as illustrated by the implementation of continuous flow reactors that can feasibly allow efficient production of suitable volumes of powdered ferrites. From the fundamental chemistry point of view, an advantage of the solution synthesis of mixed-metal oxides can lie in the control of distributions of substituent metal cations in solid solutions or during isomorphous replacement. This may allow formation of atomically homogeneous materials, or, on the other hand, the intentional construction of core-shell particles, thus allowing tuning of properties beyond chemical composition and crystal structure. A second benefit of solution crystallisation lies in the possibility of control of crystal morphology with size from the nanoscale to the micron-scale and shape from isotropic spheres and cubes, to highly isotropic rods and plates and multifaceted intricate structures. This can provide novel

materials, for example, in the study of nanoscale confinement effects in electronic and magnetic properties, or for use as additives in composites, as well as with surface properties tuned for catalysis.

We hope that our collection of examples will promote further research in this fascinating field, which represents an exciting playground for inorganic materials synthesis. The implementation of syntheses for pursuing anisotropy and shape-control in crystal form is particularly appealing, which is relevant for many applications, such as in heterogeneous catalysis, nanocomposite formation and nanotechnology, as well as in processing of powders towards real applications. Hydrothermal and solvothermal methods uniquely allow the direct formation of oxide materials from solution under very mild conditions, without the use of the extreme temperatures needed for classical oxide preparation. While this is highly advantageous for particle growth, this may mean that only certain compositions and structure are accessible since crystallisation is under strictly kinetic control, without forcing high temperatures to reach all possible stoichiometries. This may be a limitation of soft-chemical methods in general, but on the other hand metastable compositions or structures may be accessible that do not survive extreme temperatures, such as the hexagonal REFeO<sub>3</sub> perovskites that irreversibly transform on heating to the classical perovskite structure. The occurrence of competing phases from a given reagent mixture as a function if temperature, time or pH is a further complication when exploring new reaction conditions, as was illustrated in the case of BiFeO<sub>3</sub>.

Predictability of synthetic chemistry and true control of crystal morphology remains in its infancy but as we have illustrated, with the exploration of a wide variety of solvents and solution additives, progress is being made to allow desired particle size and shape in mixed-oxides to be achieved. The examples we have selected from the literature show how particle morphology can be tuned from the nanoscale to the microscale from highly facetted to anisotropic crystals, but for most of these cases the mechanism of crystal engineering is unknown and not even speculated. Much further work is needed to establish crystal growth mechanism, and this must include both experimental and computation approaches. This leads to the possibility of tailor-made materials with desirable functional properties selected by synthetic chemistry in convenient and scalable processes.

## Conflicts of interest

There are no conflicts to declare.

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