A halide free route to the manufacture of microstructurally improved M ferrite ($BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$) fibres

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Abstract

In hexagonal ferrite precursor fibres halide was found to be retained up to high temperatures, delaying the formation of the BaM ($BaFe_{12}O_{19}$) and SrM ($SrFe_{12}O_{19}$) phases, and resulting in a product with a grain size of 0.5–1 μm. This paper reports a halide free route for these fibres, using a nitrate stabilised sol precursor, from which the M phases formed at lower temperatures with smaller grain sizes. This sol was characterised and compared to the halide based sol, the evolution of the crystalline phases was studied and the hysteresis loops of the M ferrite fibres assessed by VSM. It was shown that retained halide inhibited the formation of the ferrite phase, as both SrM and BaM formed at a temperature 200 °C lower than in the halide containing precursor fibres. The grain sizes were accordingly lower, the SrM grains being below 100 nm, although the crystallite sizes were only slightly smaller than those reported for the halide containing fibres fired to 1000 °C, and the magnetic properties were also similar. The BaM fibres had $M_s = 58.4$ kA m^2 g^{-1} and $H_c = 401$ kA m^{-1}, while the SrM fibres had $M_s = 65.0$ kA m^2 g^{-1} and $H_c = 440$ kA m^{-1}, comparable to small grained polycrystalline powdered samples. The M ferrite phase was formed directly from haematite, with no $BaFe_2O_4$ observed as an intermediate, and the pure ferrites were made from stoichiometric precursors. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Globally the hexagonal M ferrites are the most commercially important magnetic materials, with a range of applications from simple permanent magnets and electric motors to memories and niche electromagnetic applications. They are magnetically hard, with high coercivities and magnetic permeabilities, and contain a high magnetocrystalline anisotropy along the c-axis of the hexagonal structure. It has been predicted that properties such as thermal and electrical conductivity, and magnetic, electrical and optical behaviour could be enhanced in material in fibrous form.[1] We have previously reported the synthesis of a range of aligned hexagonal ferrite fibres, including BaM ($BaFe_{12}O_{19}$)[2] and SrM ($SrFe_{12}O_{19}$)[3], blow spun from an aqueous inorganic sol–gel precursor stabilised by halide ions, and these were characterised physically and magnetically. These sols contained both chloride ions, retained from the iron(III) chloride precursor material despite several washes, and bromide ions from the HBr peptising agent. The precise compositions and decomposition of these fibres have been investigated and reported previously.[4]

However it was found that a relatively high temperature of 900–1000 °C was required to form the pure ferrite phase, resulting in a well-sintered product but with grains as large as 1 μm in diameter. Whilst these temperatures and grain sizes were low compared to standard ceramic methods, they were surprisingly high for a sol–gel derived product. It was suspected that the formation of the ferrite phases was restricted by the retention of halide (both Cl$^-$ and Br$^-$) ions in the fibre up to 1000 °C,[4] and so it was decided to produce fibres from a nitrate stabilised analogue of the halide based sol. It was hoped that these would form the ferrite phase at a lower

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temperature, with a corresponding reduction of grain size resulting in a mechanically superior fibre product.[5]

BaM and SrM have high saturation magnetisations (M_s) of 72 kA m^2 g^{-1} [1] and at least 74.3 kA m^2 g^{-1} respectively.[6] They also have high magnetocrystalline anisotropies along the c-axis,[1] this uniaxial character producing large theoretical maximum coercivities (H_c) of up to 594 kA m^{-1}, although polycrystalline samples rarely approach these high values.[7] The M ferrite fibres made from halide containing routes had high values for both M_s and H_c, despite their large grain sizes which approached the domain size of 1 μm.[8] Therefore the effect of reducing grain size upon the magnetic properties of the M ferrite fibres was also investigated.

2. Experimental

2.1. Sol preparation and spinning

The precursor sol was made in a method similar to the of the previously reported halide stabilised iron(III)oxyhydroxide ($FeO_{1-x}OH_{1+2x}$) sols.[2,3] A solution of iron (III)nitrate nonahydrate was precipitated with 4% ammonia solution until the mixture had reached a pH of 5. The resulting thick brown precipitate was filtered, washed and then peptised over 24 h with nitric acid, after which time there was no further significant decrease in the average sol particle size. The resulting sol had a concentration of 10.11% Fe^{3+} by weight (1.8 M). To make the M ferrite precursor sols stoichiometric amounts of $Ba(NO_3)_2$ or $Sr(NO_3)_2$ solutions were added to the iron(III)oxyhydroxide sol. Prior to spinning a small amount of polyethylene oxide spinning aid was added, and the sol was then concentrated, blow spun and collected as random gel fibres using a technique based upon a proprietary blow spinning process.[9]

2.2. Heat treatments

All gel fibres were dried immediately after spinning at 110 °C, and stored at this temperature until subsequent firing. The fibres were fired to 400 °C at a rate of 100 °C/ h, and kept at that temperature for 3 h to allow all the organic material to be removed. All samples were then fired to the desired temperature at 200 °C/h.

2.3. Characterisation

2.3.1. Photon correlation spectroscopy (PCS)
The particle sizes of the sols were measured on a Malvern Instruments Lo-C Autosizer and series 7132 multi-8 correlator at an angle of 90°, using a 4 mW diode laser, 670 nm wavelength at 20 °C. The PCS had been certified by the manufacturers to measure inorganic colloidal species of 3 nm diameter and above, provided

the difference between the RI of the solvent and particle was sufficiently large. This was the case with our samples, the RI used being 1.33 for the solvent (water) and 1.89 for FeOOH. This piece of equipment conformed to the Methods of Particle Size Determination Standards ISO 13321, part 8—PCS (1996) and BS3406, part 8—PCS (1997) for determination of the Z average calculated from the monomodal cumulants analysis. The volume and number distribution particle sizes and ranges were calculated from the cumulants results using the Malvern PCS software version 1.32 with contin algorithms. The volume distribution is a measure of the volume occupied by particles against their size, and the number distribution is a simple assessment of the particle size distribution, and these two values most accurately reflect the true nature of the sol.

It must be considered that as the PCS technique is unable to detect particles below the 3 nm threshold, these measurements may be higher than the actual true figures. Also the sols were much too concentrated to be measured undiluted, and samples were made up typically as five drops of 10.5% Fe^{3+} filtered sol in 2–3 cm^3 of water filtered through a 0.7 μm filter. This dilution did not destabilise the sols, and they showed no change over 1 day after being diluted.

2.3.2. X-ray powder diffraction (XRD)
XRD patterns of the samples treated at various temperatures were recorded in the region of $2\theta = 10$–$80°$ with a scanning speed of 0.25° min^{-1} on a Philips PW1710 diffractometer using CuK_α radiation with a nickel filter. Philips APD 1700 software was used to calculate the average size of the crystallites in a sample using the Scherrer equation:

$$D = K\lambda/h_{1/2}\cos\theta$$

where D = average size of the crystallites, K = Scherrer constant (0.9×57.3), λ = wavelength of radiation (1.5405 Å), $h_{1/2}$ = peak width at half height and θ corresponds to the peak position. BaM powder samples made from standard ceramic methods were used as reference standards, and the Philips JPDS files were used for the reference patterns.

2.3.3. Scanning electron microscopy (SEM)
Scanning electron micrographs and analysis of the morphology of the samples was carried out on a Cambridge Instruments Stereoscan 90 SEM operating at 5–10 kV. Conducting samples were prepared by gold sputtering fibre specimens.

2.3.4. The vibrating sample magnetometer (VSM)
Magnetic measurements were taken on a Maglab VSM with a helium cooled 12 T (1 T = 796 kA m^{-1}) superconducting magnet, supplied by Oxford Research

Instruments. The apparatus was controlled by six independent Oxford units, which were managed by, and the data collected using, Oxford Object Bench software. The equipment was calibrated using a high purity ($>99.99\%$) nickel sample supplied by Oxford for use in calibration when measured in a fixed field of 0.6 T at 300 K, with a stated moment of 0.350 emu at 0.6 T.

2.3.5. VSM sample preparation and accuracy

A small mound of random ferrite fibre 3×3 mm square was weighed to ±0.1 mg, placed on a piece of tissue paper, and soaked liberally with a casting resin, the surplus being absorbed by the tissue paper. This was then allowed to dry, trimmed to give a rigid square 1 mm wider than the fibre sample and mounted on a PEEK sample holder and secured with PTFE tape. Oxford Research Instruments state that the VSM is capable of producing reproducible results with an accuracy of 0.5% with a physically matched sample being measured at a fixed field over 1 hour. Errors in the weighing of the samples were crucial, since the equipment only measured the sample moment in emu, and M_s and M_r are expressed in units such as kA m^2 g^{-1} (1 kA m^2 g^{-1} = 1 emu g^{-1}) to have relevancy. The random fibre samples weighed at least 5 mg, so that the percentage error in the weight was below 1% for random fibres. All samples demonstrated an excellent reproducibility even when removed from the sample holder and remounted.

3. Results and discussion

3.1. Sol characterisation and stability

When spinning gel fibres from an inorganic sol, the existence of any large species, even in small numbers, inhibit spinning, block spinnerets and cause shot to form, resulting in a poor quality fibre product. Also very important for spinning is the degree to which the sol can be concentrated without flocculating or gelling, the minimum and optimum levels varying with each sol, but generally requiring at least 10 wt.% metal ions.

It has been found that the ferrite precursor sols usually require a volume distribution upper limit of <50 nm and a concentration of at least 13% Fe^{3+} to be spinnable, much stricter requirements than those normally needed in sol-gel work. A nitrate-stabilised iron(III) sol was successfully produced which was stable up to a maximum concentration of 23.5% Fe^{3+}, beyond which point it started to precipitate, and at which point it had a viscosity of 16 poise. Not only was this a lower maximum concentration than the 36.5% Fe^{3+} of the halide based sol reported previously, but the nitrate sol was much more viscous and "muddy" looking at equivalent concentrations, and was only stable for

around a year when stored as 10.5% Fe^{3+}. The halide based sol was stable up to a concentration of 36.5% Fe^{3+} and had a lifetime of at least 4 years when stored as 10.5% Fe^{3+}, suggesting that the halide ions actually help to stabilise the sol more than other counterions. NO$_3^-$ counterions have been found to elongate α-Fe$_2$O$_3$ sol particles to 100–200 nm, compared to spheres under 100 nm when using Cl$^-$ counter ions,[10] and clearly are less beneficial than halide counterions to iron(III)oxyhydroxide sols.

The number and volume distributions of the halide and nitrate sols are compared in Figs. 1 and 2, and it can be seen that the upper limits of both were smaller in the halide sol. This had a number average particle size of 5.1 nm, which compared well to previously reported FeOOH sols, but the volume average, which was more relevant for spinning, was slightly higher at 6.0 nm. As can be seen in Table 1, the nitrate sol had larger average particle sizes and upper limits than the halide sol. The nitrate sol had a Z average of 6.8 nm and a polydispersity of 0.658, and the PCS plots are shown in Fig. 3. Although the volume average was only slightly larger at 7.8 nm, it had an upper limit more than 50% higher at 31.5 nm, with 2.5% over 19 nm. The number distribution was closer to that of the halide sol, with an average of 6.4 nm and an upper limit of 15.7 nm. The relatively larger amount of higher volume material accounts some of the differences observed in stability and spinnability of the nitrate sols.

In the nitrate sols, nitrate salts were used to make the stoichiometric M sols. However, the barium doped nitrate sols proved to be much less stable than the halide sols regarding both stability and spinning, partly due to the relatively poor (86 g l^{-1}) solubility of Ba(NO$_3$)$_2$. The
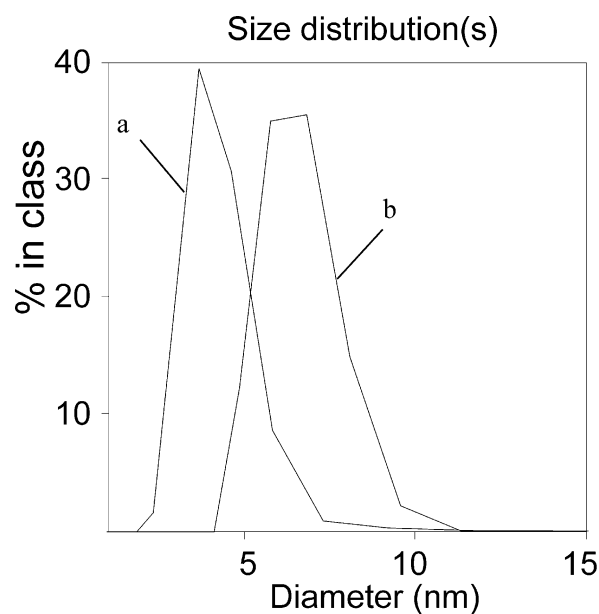

Fig. 1. Comparison of the particle size number distributions of (a) halide and (b) NO$_3^-$ stabilised iron (III) sols.
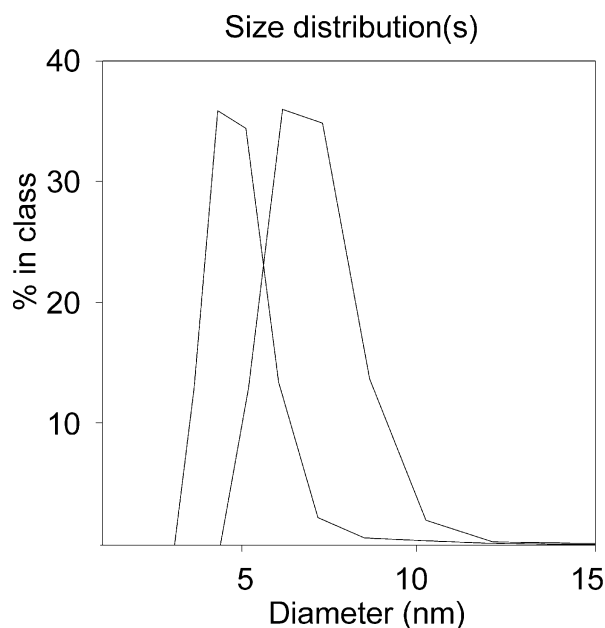
Size distribution(s)

Fig. 2. Comparison of the particle size volume distributions of (a) halide and (b) NO_3^- stabilised iron (III) sols.

Size distribution(s)

Fig. 3. Comparison of the particle size number distributions of the halide free sols, for (a) SrM and (b) BaM.

Table 1
Comparison of halide and nitrate stabilised iron(III) sols, at a concentration of 10.5% Fe^{3+}

Sol	Halide	Nitrate
Z average (nm)	4.7	6.8
Volume average (nm)	6.0	7.8
Volume upper limit (nm)	20.0	31.5
Number average (nm)	5.1	6.4
Number upper limit (nm)	14.2	15.7
Polydispersity	0.760	0.658
Max. concentration (%Fe^{3+})	36.5%	23.5%

higher Ba^{2+} doping levels which would be needed for other hexagonal ferrites, such as Co_2Z ($Ba_3Co_2Fe_{24}O_{41}$) or Co_2Y ($Ba_2Co_2Fe_{12}O_{22}$), would have resulted in an unspinnable sol. When a BaM sol was made from the nitrate sol, not unsurprisingly problems were encountered with stability and particle growth upon addition of barium, and a crown ether chelating ligand had to be added to render the sol stable at spinnable concentrations. The volume distribution had an average of 54 nm with 99.0% between 36 and 143 nm and an upper limit of 282 nm, rendering the sol almost unspinnable. The number average was similar at 49 nm, but both the range of 99.4% within 37–72 nm and the upper limit of 120 nm were proportionately much lower, although still a massive increase, caused by the barium addition (Fig. 3). Some gel fibres were collected, but they were of poor quality, contained large amounts of shot, and spinning eventually ceased as the spinnerets were blocked by the few large particles.

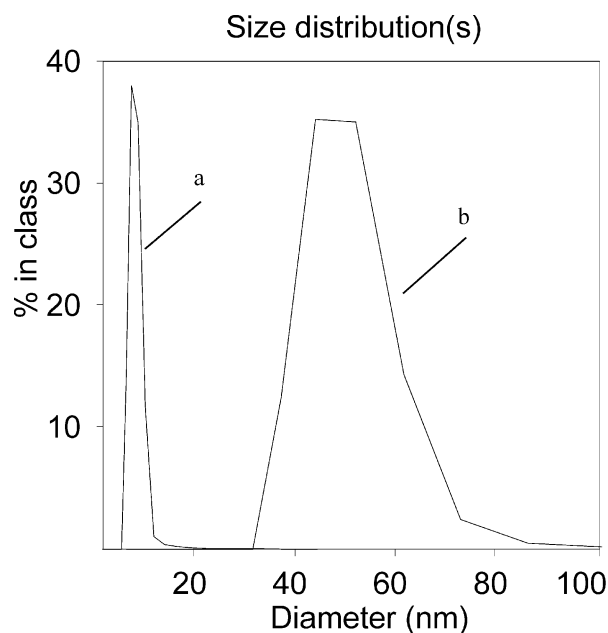Strontium nitrate is much more soluble than barium nitrate, and the SrM precursor sol could be made with-

out any stabilising additives. The nitrate based SrM sol was almost identical to the undoped nitrate sol, and was stable to over 17% Fe^{3+}. The volume average was 8.0 nm, with an upper limit of 27.2 nm and 99.1% within 5.7–15.8 nm, while the number distribution was 99.3% within 5.7–11.2 nm, with an upper limit of 18.7 nm. The lack of very small particles below 5.7 nm gave the mean peaks a narrow distribution, and this sol is contrasted to the nitrate BaM sol in Fig. 3. The sol spun easily, and appeared to be a viable SrM ferrite precursor, unlike the nitrate based BaM sol. The increased stability of the strontium doped nitrate sols allowed the opportunity to synthesise ternary sols using an all nitrate system, but again these proved much more difficult to spin than the halide based sols, and were abandoned.

3.2. Crystallisation and development of the ferrite phase

The halide free fibres produced from the nitrate-based sol confirmed the effects of halides in hindering BaM formation. At 600 °C the only crystalline phase in the fibres was haematite, but by 650 °C BaM was the major phase at ~75% with a crystallite size of 43 nm. It had formed the pure ferrite at 750 °C, with a crystallite size of 52 nm (Fig. 4). Crystalline $BaFe_2O_4$ is usually reported as forming before or at the same time as BaM, and it has been thought to be an essential precursor to the M phase. It was never observed in the halide containing M ferrite precursor fibres however, and this was attributed to the barium being associated with halides, thus preventing the formation of $BaFe_2O_4$ and delaying the crystallisation of BaM until the halides had been removed by heating to 800–1000 °C.[4] The absence of

$BaFe_2O_4$ in these halide free fibres indicates that this phase is not necessary for the formation of BaM, and that the direct transformation of haematite into BaM is a feature of this particular sol-gel fibre process, independent of which counterions are used to stabilise the precursor sol. The inhibitory effects of halide ions on M formation were proven however, as BaM both began to form and became the single phase material at a temperature 200 °C lower than in the halide containing fibres. This resulted in a product with a smaller grain size of up to 0.5 μm in diameter when fired to 750 °C, half the size of the grains in the halide containing fibres fired to 1000 °C, although the crystallite size was only 15% lower. This compares well with powdered BaM made from an alkaline sol-gel route involving the evaporation of glycol containing coprecipitated salts, in which it was found that a non-stoichiometric mixture was needed, and a ratio of Fe:Ba of 10.5 gave M ferrite at 900 °C/1 h with a grain size of 200 nm [11]. Powdered BaM has been produced from an acid sol by dissolving precipitated and washed iron(III) hydroxide in a citric acid solution at 60 °C, to which $BaCO_3$ was added in the ratio Fe:Ba = 11.6. After prefiring to remove the organic components this produced single phase BaM at 750 °C which consisted of hexagonal crystals in a narrow diameter range of 90–110 nm, and subsequent annealing had little effect on the grain size.[12]

Unfortunately, due to the problems encountered in spinning this sol detailed above, the fibres were poor with uneven sides, narrow diameters (2–3 μm), and many cracks and splits in the surface of the fibres (Fig. 5). Although it had formed pure BaM at a lower temperature and hence with a smaller grain size, from a stoichiometric precursor, the product was otherwise mechanically inferior to the halide-containing fibres, and was not well sintered.

The potential advantage of SrM was that gel fibres could be more easily spun from a nitrate stabilised sol, due to the superior sol characteristics, and indeed the resultant fibres were much better than for BaM, being comparable to the halide containing fibre reported previously. As with the halide free BaM fibre, the phase changed suddenly from only α-Fe_2O_3 at 650 °C to pure SrM at 700 °C with a crystallite size of 53 nm (Fig. 6),
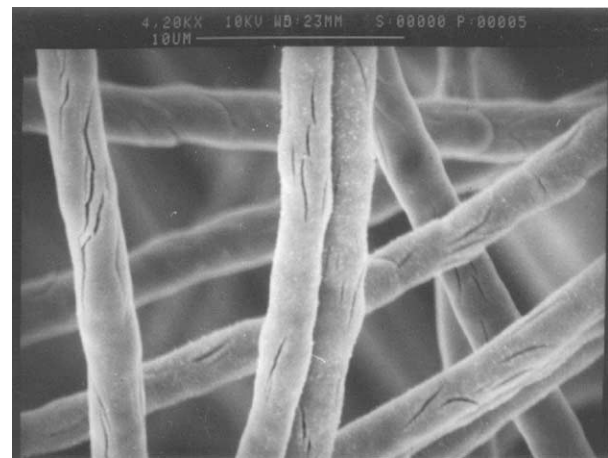

Fig. 5. SEM micrograph of BaM fibres produced from a halide-free precursor, and fired to 700 °C/3 h.
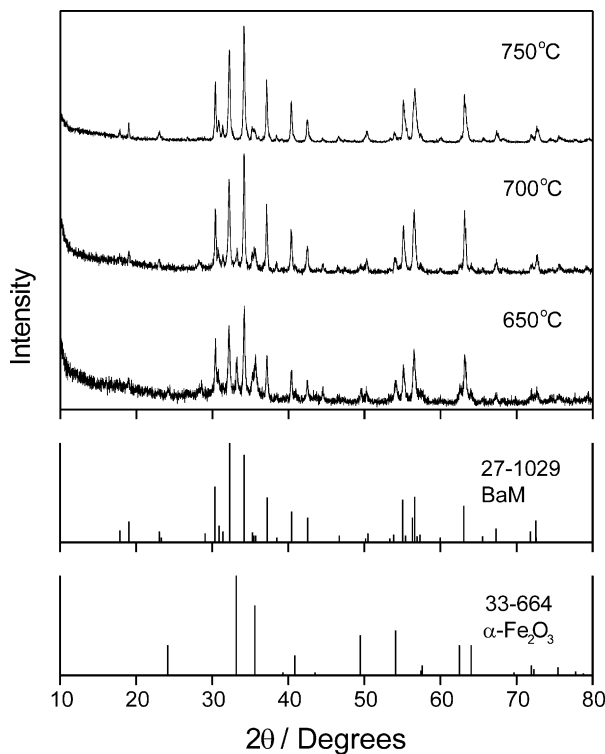

Fig. 4. XRD patterns of BaM fibres produced from a halide-free precursor, fired to 650, 700 and 750 °C/3 h.
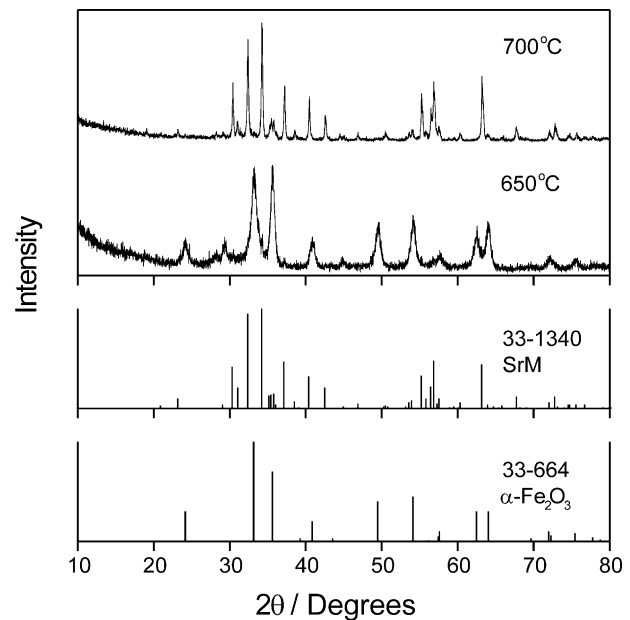

Fig. 6. XRD patterns of SrM fibres produced from a halide-free precursor, and fired to 650 and 700 °C/3 h .

without any other crystalline phases being observed except for a minor unidentified peak around 29.5 °C. This was seen previously in the halide-containing SrM fibres, and had been attributed to an unidentified strontium halide compound, but this was clearly not the case in these halide free fibres. It does not resemble any known SrO·Fe$_2$O$_3$ compound, and for now remains an unidentifiable feature of this system. An investigation of the synthesis of SrM from coprecipitated salts fired at 800–1100 °C showed that the M phase only forms as a pure product in a non-stoichiometric mixture, with an Fe:Sr ratio no more than 9, the best product requiring a ratio of 8,[13] which is even lower than required to form BaM. However, when made from a sol-gel precursor
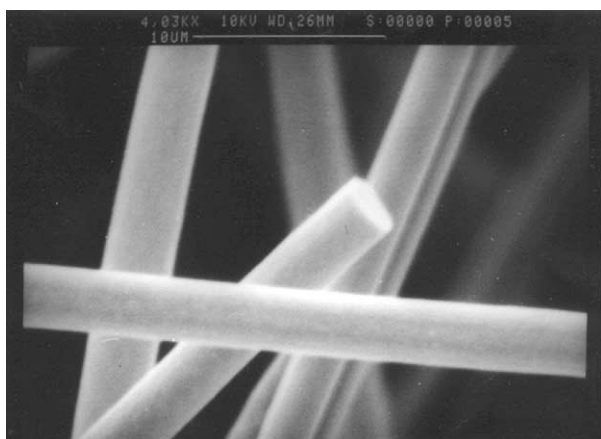

Fig. 7. SEM micrograph of SrM fibres produced from a halide-free precursor, and fired to 700 °C/ 3 h.

with a stoichiometric composition, the M phase was obtained mixed with a small amount of α-Fe$_2$O$_3$ between 800 and 1000 °C. The single phase material when fired to 1200 °C had magnetic properties comparable to those found in standard ceramic materials.[14]

In the halide free SrM fibres the single M phase was formed 50 °C lower than in the BaM fibres, mirroring the results seen for the halide containing M fibres, and this was attributed to differences in the mobility of the Sr^{2+} and Ba^{2+} ions. The SrM fibres also had a smaller grain size at equivalent temperatures than BaM, and no microstructure was seen at all in these fibres (Fig. 7), until 900 °C at which point grains on the edge of the resolution of the SEM (0.1 μm) had appeared. Again this paralleled results found in the previously reported M fibres, and the even greater difference observed here between the SrM and BaM fibres could be due to differences in particle size in the precursor sols and gel fibres. However, as with the BaM fibres, the SrM fibres were not well sintered at this temperature, and would require further densification to optimise their magnetic properties.

3.3. Magnetic measurements

The magnetic hysteresis loops of random BaM and SrM fibres made from nitrate stabilised sols are shown in Fig. 8. Magnetically the nitrate based route demonstrated little change from the halide route, which gave an M_s of around 63 kA m^2 g^{-1} and H_c of around 0.5 T (398 kA m^{-1})[8] despite the difference in grain size
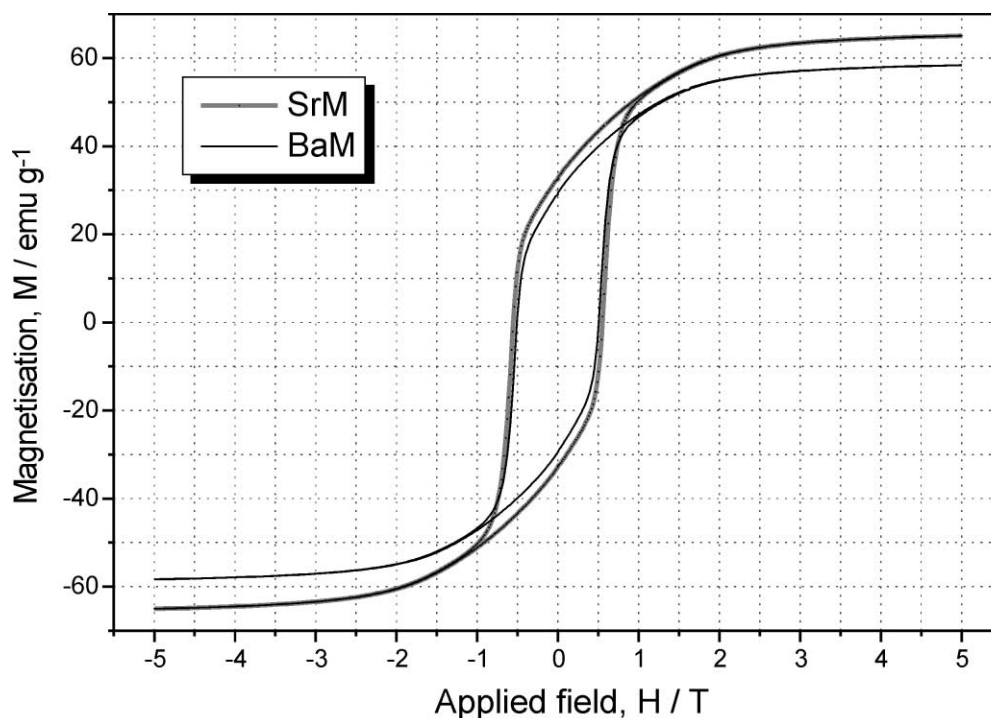

Fig. 8. Hysteresis loops of random BaM and SrM fibres made from halide free sol precursors.

between the two routes. The BaM fibres were slightly inferior to those from the halide route, with $M_s = 58.4$ kA m^2 g^{-1} (1.0% error) and $H_c = 0.504$ T (401 kA m^{-1}), whereas the SrM proved slightly better, with $M_s = 65.0$ kA m^2 g^{-1} (0.7% error) and $H_c = 0.553$ T (440 kA m^{-1}). The crystallite sizes of both M fibres were similar to those of the halide fibres after being fired 1000 °C/3 h, but their grain sizes were drastically different, with no grain structure over 0.1 μm in the nitrate stabilised fibres. However, despite this, the magnetic properties of the fibres were similar, indicating that crystallite size and not grain size largely determines M_s and H_s, as long as the grains are below domain size and above paramagnetic dimensions (between 0.05 and 1 μm).[6] Due to their slightly higher formation temperature and poor morphology, with cracks in the uneven surface of the fibre, the BaM fibres could be more porous than the SrM fibres, thus lowering their M_s accordingly.

4. Conclusions

A nitrate stabilised, halide free iron(III)hydroxide sol was synthesised, characterised, and compared to the halide stabilised sol reported previously, and was shown to have a 30% larger volume average particle size of 7.8 nm, with an upper limit 50% higher than the halide stabilised sol. While this would not be a problem in normal sol-gel work, for blow spinning an average size of over 50 nm has been found to be detrimental to spinning. Upon addition of stoichiometric amounts of Sr(NO$_3$)$_2$, the SrM precursor sol suffered little change, and resembled the halide stabilised, halide-salt doped sols used previously to manufacture a range of hexagonal ferrite fibres, with a volume average of 8.0 nm and an upper limit of 27.2 nm. However, addition of stoichiometric Ba(NO$_3$)$_2$ resulted in a large increase in particle size to 53.8 nm with an upper limit of over 280 nm, caused by the relatively low solubility of Ba(NO$_3$)$_2$, rendering this sol nearly unspinnable. Nevertheless random gel precursor fibres were collected for both SrM and BaM, although the BaM fibres were of poor quality and spinning was difficult, and higher doping levels would be impossible.

It had previously been supposed that halide retained within the fibre to high temperatures was inhibiting the formation of the ferrite phase, and this was shown to be the case as both SrM and BaM formed at a temperature 200 °C lower than in the halide containing ferrite fibres. The grains were accordingly smaller, especially in the case of the SrM fibres, which had a grain size of below 100 nm, although the crystallite sizes derived from XRD were only 10–15% less than those reported previously. The M ferrite phase was formed directly from haematite, with no BaFe$_2$O$_4$ observed as an intermediate, and the pure ferrites were made from stoichiometric precursors. The magnetic properties were found to be very similar to those of the halide containing fibres fired to 1000 °C, despite the much reduced grain sizes, indicating that crystallite size rather than grain size determines the magnetic characteristics, as long as the grains are below domain size and not small enough to become paramagnetic. The BaM fibres had $M_s = 58.4$ kA m^2 g^{-1} and $H_c = 401$ kA m^{-1}, while the SrM fibres had $M_s = 65.0$ kA m^2 g^{-1} and $H_c = 440$ kA m^{-1}, comparable to small grained polycrystalline powdered samples.

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