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Convenient, low energy routes to hexagonal ferrites $MFe_{12}O_{19}$ ($M = Sr, Ba$) from SHS reactions of iron, iron oxide and MO_2 in air†

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Thermal initiation of a mix of metal superoxide (MO_2, M = Sr, Ba), iron and iron powder in air induces a self propagating reaction with velocity 0.5 mm s^{-1} and the formation of predominantly $MFe_{12}O_{19}$. Heating the mixture to 1150 °C for 2 h produces pure crystalline $MFe_{12}O_{19}$. The ferrites were characterised by X-ray powder diffraction (Rietveld analysis), FTIR, VSM magnetism, EDAX/SEM, electron probe analysis and Mössbauer spectroscopy. The ferrites showed good purity, coercivity, remanence and hysteresis loops compared to commercial samples. Preparation of ferrite solid solutions $M_xM'_yFe_{12}O_{19}$ (M = Sr, Ba, Pb) was investigated.

Hexagonal ferrites $MFe_{12}O_{19}$ are found in nature,[1] for example magnetoplumbite $PbFe_{12}O_{19}$. Most are ferrimagnets but some are antiferromagnetic. The most studied member of this class of materials is hexagonal barium ferrite which is extensively used as a permanent magnetic material, it is known commercially as Ferroxdure. Hexagonal ferrites are widely used as they have high Curie temperatures (500–800 K), are insulators, have strong magnetic anisotropy and high coercivities (300 Oe).[1] Some hexagonal ferrites have magnetisation within the basal plane of the structure, known as Ferroxplanes. Hexagonal ferrites are one of the three major classes of 'ferrites' the other two being the spinel ferrites, $MO{\cdot}Fe_2O_3$, which are soft magnets used in transformers, and garnets, $M^{III}{}_3Fe_5O_{12}$, which are used in microwave devices. Of the three classes the spinel ferrites are perhaps the most studied in chemistry whilst the hard hexagonal ferrites find the widest range of applications as permanent magnets.[1]

Barium ferrite was first introduced in 1952 by Philips Laboratories.[2] It has the magnetoplumbite structure and in addition to its current commercialisation shows potential in advanced magnetic recording applications such as high definition video and flexible discs because of high recording density and low manufacturing costs.[3] Ferrites can be formed in corrosion processes[4] however the conventional preparation method involves the reaction of barium carbonate and iron oxide at high temperatures for prolonged time periods.[5] This procedure can lead to large agglomerates with inhomogeneous composition. Indeed conventional processing of the ferrite materials can involve twelve separate steps.[5] New synthetic methods to hexagonal ferrites involve some sort of modified Pechini,[6] nitrate or citrate type method.[7]

We have been looking at non-conventional synthesis of inorganic oxides *via* reactions that are self-propagating and self-energetic.[8] These processes are driven by an exothermic chemical reaction which provides both the precursor elements for the final ceramic and the energy for the process; alleviating the need for a furnace. These reactions were initially developed in Russia by Merzhanov and co-workers and are called self propagating high temperature synthesis or SHS.[9] The most commonly known example of an SHS reaction is the thermite reaction which is used to join railway tracks. Commonly SHS reactions use the elements or element oxides as the starting materials:

$$M + E \rightarrow ME \qquad (M = \text{metal}, E = \text{non-metal}) \tag{1}$$

Initiation can be achieved by a hot wire, this promotes a propagation wave (solid flame) which passes through the ceramic compact, generating extremely fast heating (temperatures up to 3000 °C in a fraction of a second) and rapid quenching.[10] Control of the reaction temperatures and particle sizes is possible by the addition of diluting agents and by conducting the SHS reaction under different gaseous atmospheres. For example, in the synthesis of mixed-metal oxides an oxygen atmosphere and elemental metals are often used. A preliminary communication on the SHS synthesis of $SrFe_{12}O_{19}$ under an oxygen atmosphere has been reported elsewhere.[11] Hexagonal ferrites have also been made by using modified redox mixtures containing hydrazine carboxylate ligands coordinated to iron. Combustion of the solution produces a vigorous exothermic decomposition of both the solute and solvent with formation of ferrites which after processing display good magnetic characteristics ($\sigma_s = 29.8$ emu g^{-1} and $H_c =$ 1925–5300 Oe).[12] We have helped develop a subset of SHS reactions called solid state metathesis reactions or SSM.[11] In these processes metal halides are used as starting materials.[13]

$$MCl_x + Na_xE_y \rightarrow ME_y + x\text{NaCl} \tag{2}$$

These reactions have in-built chemical control over the reaction temperature, with the latent heats of melting and vaporisation of the co-products (such as NaCl) acting as a heat brake.[14]

Here we report a new, inexpensive, single step, solid-state route for the preparation of hexagonal ferrites in air *via* SHS reactions.

Experimental

All reagents were obtained from Aldrich Chemical Co. and checked for phase and elemental purity by X-ray powder diffraction (XRD) and energy dispersive X-ray analysis (EDXA) prior to use. Manipulations, weighing and grindings were performed under a nitrogen atmosphere in a Saffron Scientific glove box. SHS reactions were carried out in air or under a flow of oxygen gas on pre-ground powders supported on a ceramic tile. Sintering was carried out on pressed pellets

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(5 tonne) using a carbolite rapid heating furnace. Heating and cooling rates were typically 20 °C min^{-1}. A commercial sample of $BaFe_{12}O_{19}$ was obtained from Sakai Chemical Industries, Osaka. XRD measurements were performed on a Siemens D5000 diffractometer in transmission mode using germanium-monochromated Cu-Kα1 ($\lambda = 1.5406$ Å) radiation and by a Philips X-pert using Cu-Kα1 radiation in the reflection mode. Reitveld analysis was performed using the FULLPROF program supplied by the Laboratoire Leon Brillouin, Saclay. Vibrating sample magnetometry were carried out on a Princeton Applied Research magnetometer at room temperature in applied fields of up to 10 kOe. The sample density ρ was taken to be 5.0 g cm^{-3} in order that the induction B could be estimated from the measurement magnetisation σ using $B = 4\pi\rho\sigma$. Curie temperatures were defined from thermal scans of the magnetisation in a field of 8 kOe. Scanning electron microscopy (SEM) and EDXA were carried out with a Hitachi S-4000 instrument and microprobe analysis on a JEOL EMA. analyser FTIR spectra were recorded on a Nicolet 205 instrument using pressed KBr discs. Transmission Mössbauer spectra were recorded on a Wissel MR-260 constant acceleration spectrometer. Spectra were recorded in 512 channels then numerically folded to remove baseline curvature and calibration was performed relative to α-Fe at room temperature. Powder samples were mounted in a circular plastic cell (2 cm diameter). Data analysis was performed with the thin absorber approximation, using Lorentzian lineshapes and assuming a first-order perturbation approach to the combination of electric quadrupole and magnetic hyperfine interactions. The spectra were fitted with a least-squares fitting program developed by one of the authors (Q.A.P.), using a constrained set of five subspectra corresponding to the five inequivalent Fe sites in $MFe_{12}O_{19}$. TG and DSC measurements were made in Russia on a SETRAM, TAG 24 thermal analyser under an oxygen atmosphere.

Preparation of $MFe_{12}O_{19}$ (M = Ba, Sr)

The same general scale and procedure was followed for both the Sr and Ba reactions outlined below for Sr.

SrO_2 (1.196 g, 10 mmol), iron powder (2.513 g, 45 mmol) and Fe_2O_3 (7.186 g, 45 mmol) were ground together in a pestle and mortar. The resulting powder was placed on a ceramic tile in air and the mixture initiated by means of a nichrome filament at 800 °C. This produced an orange propagation wave that travelled through the material at *ca.* 0.5 mm s^{-1}. The powder darkened to black after the propagation wave had passed and became partly fused. The black material both as prepared and after pressing and sintering at 1150 °C for 2 h was analysed by X-ray powder diffraction (Table 1), VSM magnetrometry (Table 2), FTIR, SEM/EDXA, electron probe analysis and Mössbauer spectroscopy. The FTIR spectra of the hexagonal ferrites showed a broad band at 600 cm^{-1}. Electron probe analysis for the sintered material gave $SrFe_{12.05}O_{19}$ and $BaFe_{12.1}O_{19}$. EDAX gave equal ratios of Sr and Ba to iron across all surface sites for the sintered material in the expected ratios. The as prepared material showed some surface inhomogeneity (*ca.* 10% unreacted starting materials).

Variations in the ratios of the starting materials were investigated with 1 : 4 and 1 : 12 ratios of MO_2 to iron mixture (equal molar ratio of Fe to Fe_2O_3). With excess MO_2 over the expected ratio, $SrFe_2O_4$ was the predominant phase, whilst with the stoichiometric 1 : 12 reaction, unreacted Fe_2O_3 was also observed. The reaction was also studied by varying the ratio of iron to iron oxide. With no iron oxide, the reaction was extremely vigorous and proceeded with a propagation velocity in excess of 1 cm s^{-1}, a white solid flame, and ejection of reaction material in a large vicinity. The product in this case was predominantly iron oxide.

Attempts to form $PbFe_{12}O_{19}$ from a comparable reaction of PbO_2 and Fe/Fe_2O_3 produced a biphasic mixture of Fe_2O_3 and a material that analysed with a Pb to Fe ratio of 1 : 23 (EDAX, electron probe).

Preparation of $M_xM'_yFe_{12}O_{19}$ (M, M′ = Pb, Sr, Ba)

Attempts at forming solid solutions of Sr/Ba; Sr/Pb and Ba/Pb ferrite were accomplished by reacting predetermined amounts of the constituent metal peroxides. The reaction scale and procedure were identical to that outlined above. It was found possible to form $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ by this method. Reactions involving PbO_2 as a starting material produced an inhomogeneous product that was shown by X-ray powder diffraction, SEM/EDAX and electron probe analysis, to consist of at least three phases; unreacted Fe_2O_3, $MFe_{12}O_{19}$ (M = Sr, Ba) and a mixed lead barium ferrite that was deficient in lead.

Reactions in an oxygen atmosphere

The same scale and reaction procedure as outlined above was carried out except the reactants were placed on a ceramic tile that was contained in a quartz tube (5 cm diameter, 25 cm long). The quartz tube was open at one end and the tube flushed with oxygen gas (2–4 l min^{-1}). The propagation velocity was 1–2 cm s^{-1} and some material was ejected from the reacting powders (*ca.* 5%).

CAUTION: SHS reactions can be very exothermic, sometimes explosively, so with any new system care should be taken to carry the reactions out behind a blast proof screen. High temperature material can be ejected from the site of a laboratory-scale reaction up to 1 m.

Table 1 Structural data for the ferrites prepared in air and oxygen compared to a commercial ferrite prepared by the standard ceramic method. Lattice parameters and impurities were determined by Rietveld analysis. R_B is the Bragg factor

sample	d/Å	$a = b$/Å	c/Å	purity	impurity	R_B(%)
commercial $BaFe_{12}O_{19}$	420(11)	5.8972(15)	23.2116(32)	100.0(1.0)	—	10.8
SHS $BaFe_{12}O_{19}$ (in air)	394(12)	5.8932(27)	23.2169(58)	97.0(1.4)	$BaFe_2O_4$	19.8
SHS $SrFe_{12}O_{19}$ (in air)	431(7)	5.8798(18)	23.0538(40)	100.0(1.6)	$SrFe_2O_4$	15.7
SHS $SrFe_{12}O_{19}$ (in O_2)	379(11)	5.8829(27)	23.0627(59)	96.7(1.7)	$SrFe_2O_4$	20.4

Table 2 Magnetic data for the ferrites. Hysteresis loops were recorded at room temperature in a field of up to 10 kOe to determine the remanent induction B_r, coercive field H_c, magnetisation s (at $H = 10$ kOe) and maximum energy product BH_{max}. Mössbauer data are shown for the hyperfine field B_{hf} and linewidth G of the sub-spectra corresponding to Fe atoms in the 12k site of $MFe_{12}O_{19}$

sample	B_r/G	H_c/Oe	s/emu g^{-1}	BH_{max}/MG Oe	T_c/°C	B_{hf}/kG	Γ/mm s^{-1}
commercial $BaFe_{12}O_{19}$	2204	2665	35.09	0.84	480	—	—
SHS $BaFe_{12}O_{19}$	2205	2660	35.10	0.74	475	415	0.39
SHS $SrFe_{12}O_{19}$	2314	2955	36.84	0.89	480	411	0.34
SHS $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$	2224	3069	35.40	0.73	475	413	0.32

Results and Discussion

An SHS reaction can be initiated by a hot filament at 800 °C between preground powders of MO_2 (M = Ba, Sr), Fe and Fe_2O_3 supported on a ceramic tile in air. This produces an orange coloured solid flame that spreads out from the ignition point with velocity of *ca.* 0.5 mm s^{-1} (Fig. 1). On passage of the flame the material darkens from a purple to a black coloration and becomes partly fused. The nature of the product and the speed of the propagation wave can be directly influenced by manipulating the ratio of the three components. The driving force for the reaction is the very exothermic oxidation

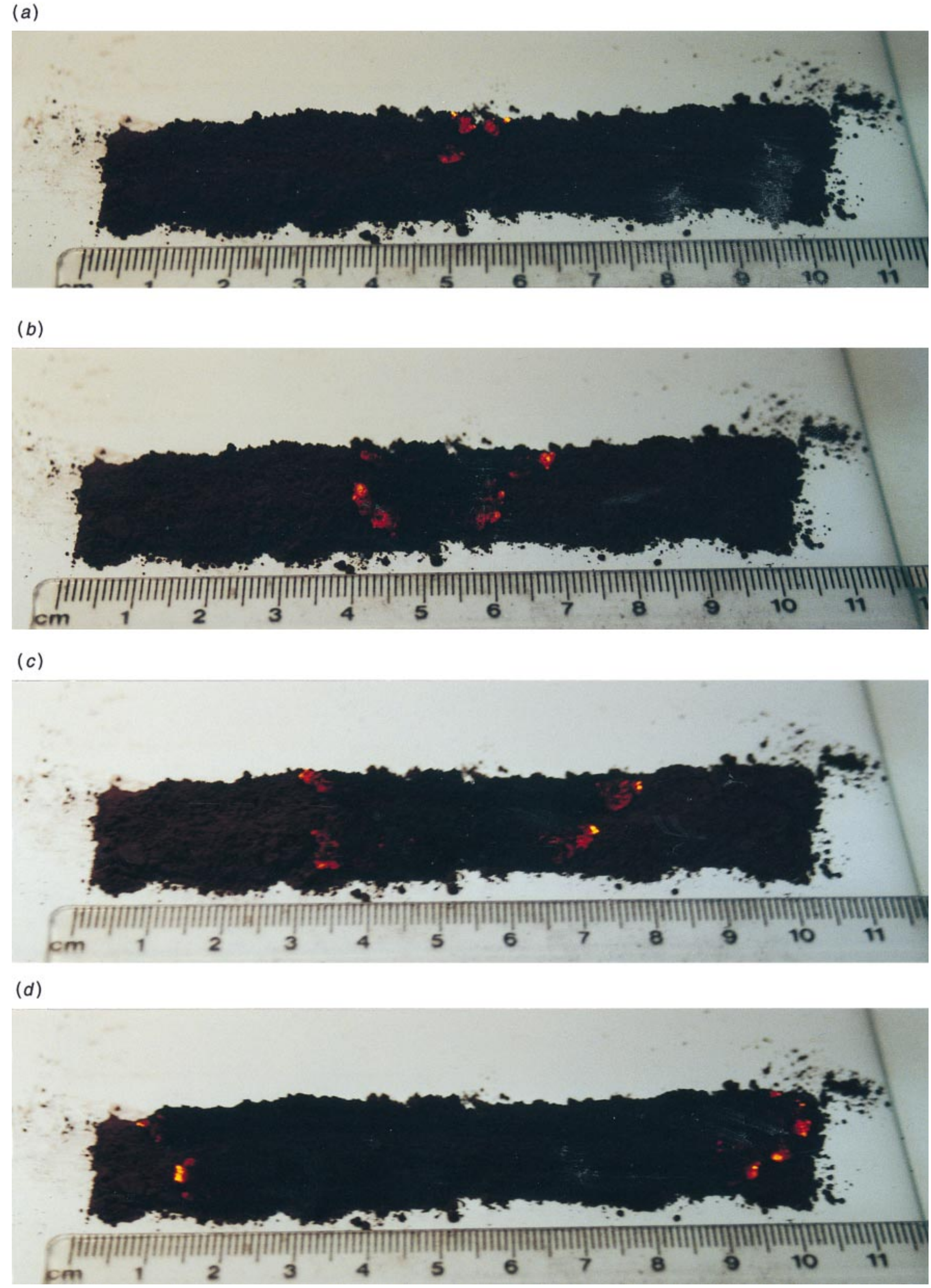

Fig. 1 Photographs of the solid flame produced on initiating a mixture of SrO_2, Fe and Fe_2O_3 (1 : 4.5 : 4.5 molar ratio) at (*a*) $t = 0$; (*b*) $t = 20$ s; (*c*) $t = 40$ s; (*d*) $t = 80$ s. The mixture was initiated by a hot filament at the center of the powder near the top, two solid flames are visible travelling to both the left and right in the photographs; scale bar is in cm.

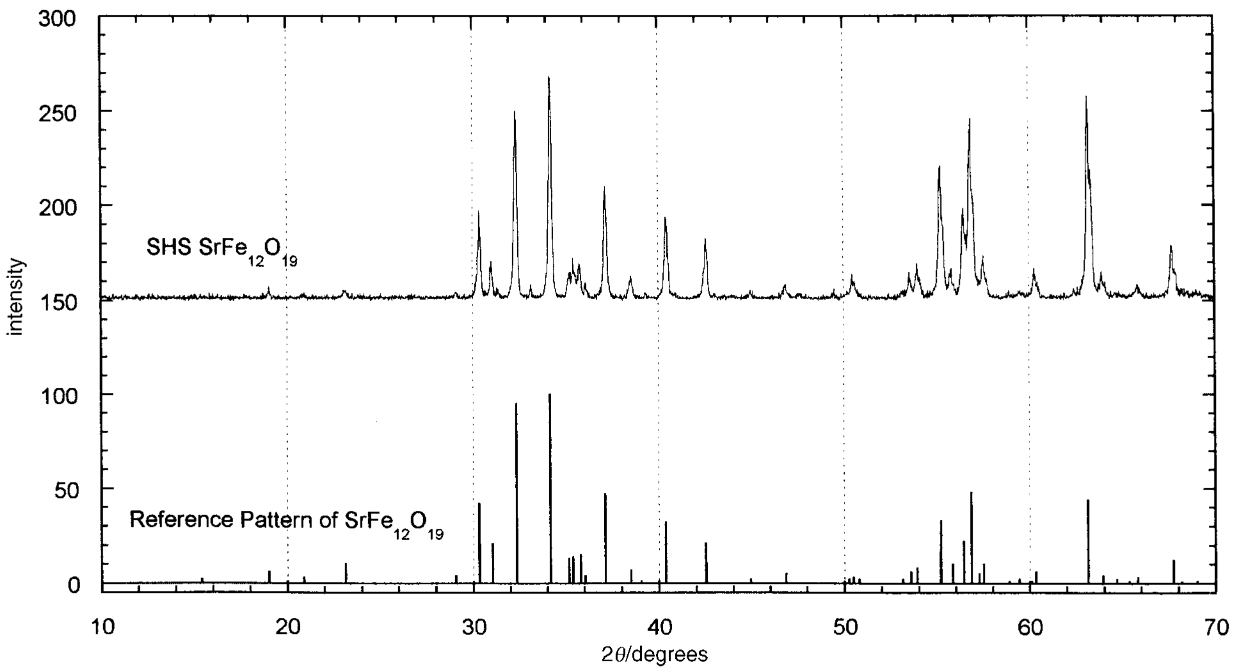

Fig. 2 Upper trace: X-ray powder diffraction pattern obtained from reaction of SrO_2, Fe and Fe_2O_3 (Sr:Fe/Fe_2O_3, 1:9) in air, after annealing at 1150 °C for 2 h. Lower trace: literature stick pattern for $SrFe_{12}O_{19}$.

of the iron metal (800 kJ mol^{-1}), the iron oxide acts as a moderator and the MO_2 as an internal oxidising agent. In the absence of the Fe_2O_3 the reaction proceeds with a velocity of *ca.* 1 cm s^{-1} with a white coloured flame and material is ejected from the reaction site. The predominant product in this instance, confirmed by powder XRD, is Fe_2O_3. Combination of the powders in the stoichiometric ratio for $MFe_{12}O_{19}$ produced the required product but also contained significant amounts of unreacted Fe_2O_3. Increasing the amount of MO_2 in the reaction mixture to a ratio of 1 part MO_2 to 9.0 parts iron (equal amounts of Fe and Fe_2O_3) produced virtually pure $MFe_{12}O_{19}$. Further increases in the ratio produced the addition of a further phase identified as MFe_2O_4. The idealised equation for the reaction is given by,

$$MO_2 + 6Fe + 3Fe_2O_3 + 4O_2 \rightarrow MFe_{12}O_{19} \quad (M = Sr, Ba) \quad (3)$$

The materials produced directly from the SHS reaction and after annealing at 1150 °C for 2 h were analysed by X-ray powder diffraction (Table 1), SEM/EDXA, Mössbauer spectroscopy, VSM and electron probe analysis. The annealed products showed better purity and magnetic orders of merit and were fully analysed as detailed below. The X-ray powder diffraction patterns for different molar ratios of reagents show that the best product was obtained from a 1:9 Sr to Fe reagent ratio, and showed an excellent match with literature patterns[15] (Fig. 2).

Rietveld analysis of the X-ray data showed that the impurity level in the product was $<3\%$ (Table 1). The following phases were tested for: $MFe_{12}O_{19}$, MO_2, Fe_2O_3, Fe_3O_4, MFe_2O_4 and MO.

Identification of the impurities was largely based on indexing the main observed non-$MFe_{12}O_{19}$ peak, at $2\theta \approx 30°$. This led to the conclusion that the major impurity in all cases was MFe_2O_4, and the data in Table 1 refers to fits obtained with two phases only, $MFe_{12}O_{19}$ and MFe_2O_4. Crystallite sizes were calculated using the Scherrer formula[16] for the 34.5° peak, which corresponds only to the $MFe_{12}O_{19}$ phase; the as prepared ferrites had sizes of order of 370–430 Å.

The FTIR spectra of $MFe_{12}O_{19}$ showed a broad band centred at 600 cm^{-1} corresponding to an Fe—O stretch. EDXA and electron probe analysis showed only Group IIa metal, iron and oxygen across all surface spots with a standardised compositional analysis of $BaFe_{12.1}O_{19}$ and $SrFe_{12.05}O_{19}$ for the annealed 1:9 powder. No evidence of the presence of the impurity detected by the Rietveld analysis could be seen, however in the barium case the composition analysis for Ba varied by *ca.* 1% over many surface spots. The annealed 1:12 molar ratio material showed some surface inhomogeneity by EDXA with variations in elemental compositions corresponding to regions of Fe_2O_3 (*ca.* 10% as assessed by electron probe analysis). The SHS ferrites had good coercivity, remanence and energy product when compared to a commercial sample (Table 2). This is illustrated in the room-temperature hysteresis loops for the 1:4, 1:9 and 1:12 materials in Fig. 3. The hysteresis loop for commercial $BaFe_{12}O_{19}$ shadows almost exactly the curve for the annealed 1:9 material. The Curie temperatures of the annealed 1:9 SHS prepared ferrites gave values between 470 and 480 °C, comparable with commercial material.

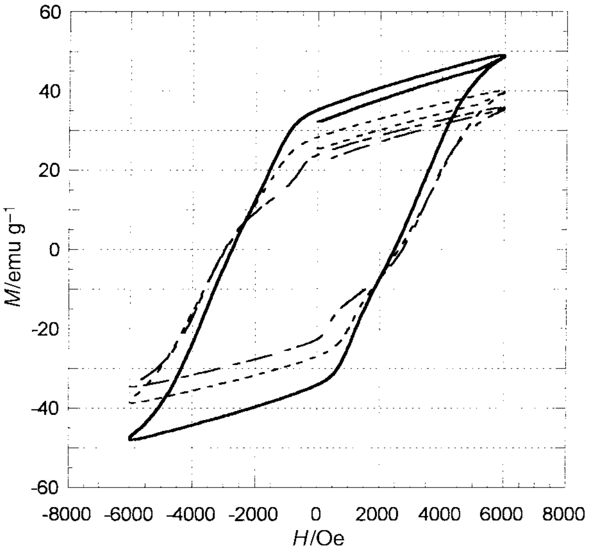

Fig. 3 Room-temperature hysteresis loops for the sintered powders (1150 °C, 2 h) prepared from 1:4 (— —), 1:9 (——), and 1:12 (- - -) Sr:Fe/Fe_2O_3 ratios

Mössbauer measurements of the 1:9 ratio material show patterns that are identical to literature measurements[17] with iron in the expected five site environments. Room-temperature spectra for the Ba, Sr and mixed Ba and Sr ferrites are shown in Fig. 4. The relative areas of the five-component subspectra were constrained in the ratio 12:2:2:4:4, as appropriate for the relative occupancies of the three spin-up sites, the 12k, 2a and 2b sites, and of the two spin-down sites, the $4f_{IV}$ and $4f_{VI}$ sites respectively. No significant Fe-containing impurities were apparent in any of the spectra.

The initial as prepared ferrites showed some inhomogeneity according to X-ray powder diffraction and by EDXA, corresponding to *ca.* 10% unreacted starting material in the reagent mixture, the predominant product in the reaction however was the required ferrite for the 1:9 ratio material. The hysteresis loops of this material show at least two components, although the overall energy products and coercivities are comparable to the annealed powders. In air, although the metal superoxide acts as an internal oxidising source it does not supply sufficient oxygen to form the required phase [eqn. (3)]. The rate of air diffusion into the reacting powders is probably the limiting factor in determining the rate of reaction propagation, phase and crystallite size of the product.

Reaction of PbO_2 with Fe and Fe_2O_3 did not produce magnetoplumbite ($PbFe_{12}O_{19}$) even with many different starting material ratios (1:4; 1:9; 1:12). The product as prepared showed a mixture of at least three phases including Fe_2O_3. The only lead-containing product showed a Pb to Fe ratio of 1:23. This phase could not be identified from the X-ray powder diffraction pattern of the powder. Sintering the as-prepared powder did not produce magnetoplumbite but did reduce the lead content of the final product.

The desired phase is not attained owing to the volatility of PbO. The propagation temperature in these reactions is of the order of 1100 °C as determined by optical pyrometry. Lead oxide (PbO) is known to have a significant vapour pressure at 800 °C, and is thus volatilised during the course of the reaction.

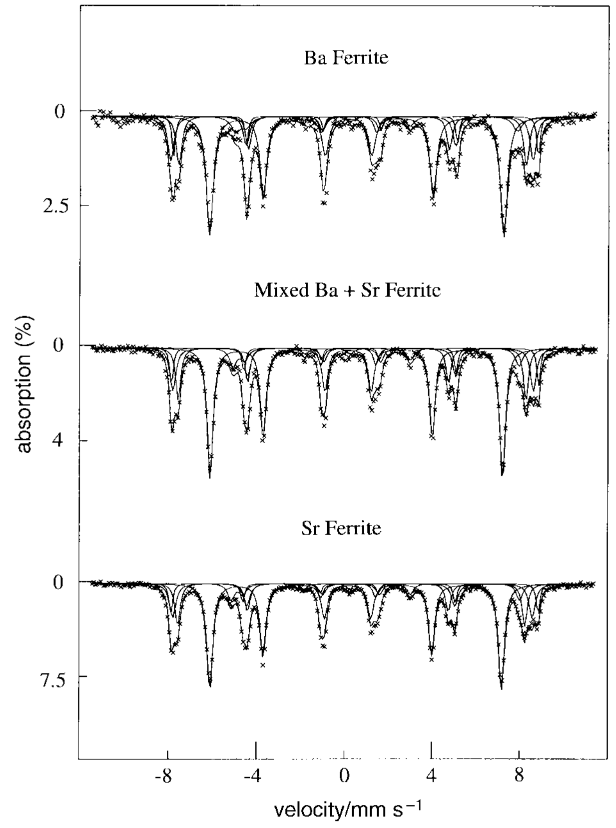

Fig. 4 Room-temperature Mössbauer spectra for sintered powders (1150 °C, 2 h) prepared from 1:9 M:Fe/Fe_2O_3 ratios for M = Ba, 0.5 Ba + 0.5 Sr, and Sr. The solid lines are least-squares fits using a constrained set of five Lorentzian sextets corresponding to the five distinct Fe sites in $MFe_{12}O_{19}$.

The reactions of MO_2 (M = Ba, Sr), Fe and Fe_2O_3 were also studied under an oxygen atmosphere. In this reaction the propagation velocity of the solid flame was faster for comparable reaction ratios than when carried out in air. The reaction temperature was also greater (yellow–white flame, *ca.* 1250 °C). The 1:9 product after annealing at 1150 °C for 2 h showed identical X-ray powder diffraction, FTIR and EDXA analysis to the reactions carried out in air. The magnetic characteristics of the materials were slightly inferior (Table 1). This may in part be due to the higher reaction temperature in the initial SHS reaction.

Attempts were made to form solid solutions of $M_xM'_yFe_{12}O_{19}$ by pregrinding mixtures of xMO_2 and $yM'O_2$ and initiating the reaction. When M and M′ were Ba and Sr it was possible to obtain a solid solution for the 1:9 reagent mixture and the materials showed good homogeneity by EDXA and electron probe mapping, correct X-ray powder diffraction pattern and comparable magnetic characteristics to $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ (Table 1). All attempts to introduce Pb into the solid solutions failed, the products were inhomogeneous, multiphase and deficient in lead (typically 10% of the expected amount of lead was observed in the products). The failure in these cases can also be related to the volatility of lead oxide.

The ratios of reactant required to produce hexagonal ferrites seem unusual with the stoichiometric reaction ratio leading to unreacted iron oxide. This can be attributed to barium or strontium loss from the reaction site owing to the volatility of the oxide. It could also be due to ejection of material from the reacting powder. The empirically determined ratio of 1:9 allowed for moderate propagation velocity and for a homogeneous product, presumably sufficient barium or strontium is available for the formation of the hexagonal ferrite at this ratio. Literature ceramic preparations of $SrFe_{12}O_{19}$ also use a molar excess of strontium, typically a 1:11 Sr to Fe ratio.[18]

DSC studies under an oxygen atmosphere of the reaction of SrO_2 with Fe and Fe_2O_3 revealed a large exotherm corresponding to an initiation temperature between 450 and 800 °C (Fig. 5). This can be correlated with the combined TG–DSC data for the individual starting components (Fig. 6). The exotherm is clearly due to oxidation of iron metal, although notably the heat flow characteristics for ferrite formation and the individual components are different. TG of the reaction shows an overall slight mass gain in the experiment (*ca.* 10% overall), this is expected because of mass gain upon oxidation of iron metal.

SHS reactions to form hexagonal ferrites are easy to perform

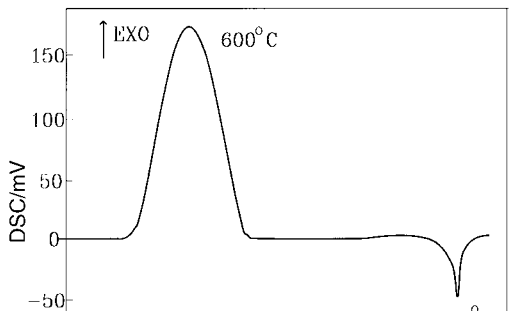

Fig. 5 DSC measurement of the reaction of Fe/Fe_2O_3 and BaO_2

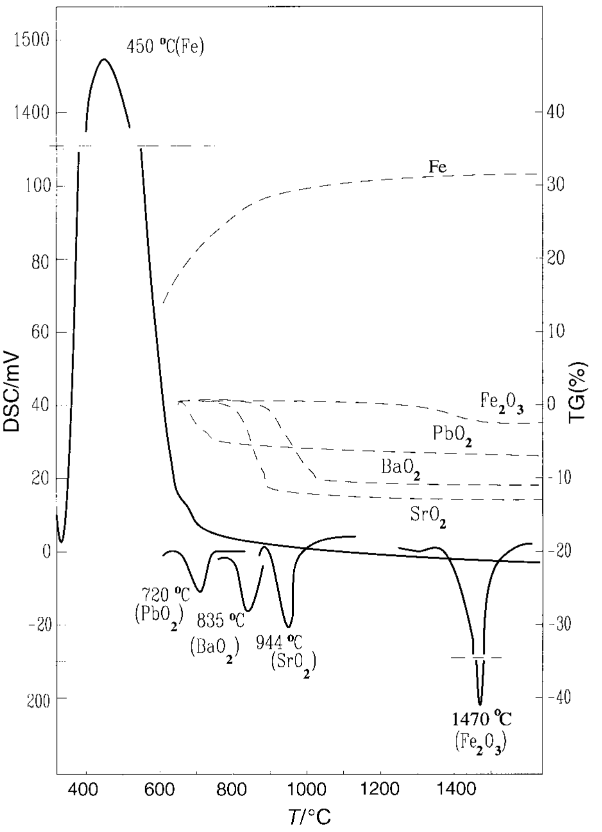

Fig. 6 Combined DSC and TG data for the reactions of Fe, Fe_2O_3, SrO_2, BaO_2 and PbO_2 in oxygen

using inexpensive starting materials and equipment, producing ferrites with far fewer processing steps than in conventional precipitation synthesis.[5] They have the advantage of forming the required product directly in the SHS reaction. Although this product does contain some impurities the required ferrite can be obtained in virtually quantitative yield by sintering the product at 1150 °C in air. An advantage of the SHS processing is the rapid heating and cooling which gives rise to metastable ferrites which are readily sintered. It is possible to promote the reaction by pressing a single disc of the starting materials and ramping the temperature in a furnace up to 1150 °C. The final product in this case is slightly inferior but involves only one step.

Conclusions

SHS reactions offer a fast, inexpensive, straightforward method of producing good quality hexagonal ferrites $MFe_{12}O_{19}$ (M = Sr, Ba) in high yield. The reaction can be carried out effectively in air without the need for special apparatus or an oxygen atmosphere. The ferrites obtained after annealing at 1150 °C are comparable to commercial samples, however the reaction involves far fewer processing steps. The reaction is promoted by the internal oxidising agent MO_2. Mixed-solid solutions of $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ could be made by this method, however all attempts to form $PbFe_{12}O_{19}$ and solid solutions containing lead were unsuccessful. This was attributed to the volatility of lead oxide (PbO).

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