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Self-propagating high-temperature synthesis of chromium substituted lanthanum orthoferrites $LaFe_{1-x}Cr_xO_3$ ($0 \leqslant x \leqslant 1$)

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Pure and chromium substituted lanthanum orthoferrites $LaFe_{1-x}Cr_xO_3$ ($x=0$, 0.1, 0.25, 0.4, 0.55, 0.7, 0.85, 1) were synthesised in air by self-propagating high-temperature synthesis (SHS): a combustion process involving the reaction of lanthanum(III) oxide, iron(III) oxide, chromium(III) oxide and iron (or chromium) metal powder. Two series of samples were produced: series 1 – SHS in the absence of an external magnetic field; and series 2 – SHS in a magnetic field of 1.1 T; both processes were followed by sintering at 1400 °C for 36 h with intermediate grinding. Scanning electron microscopy, energy dispersive analysis of X-rays, X-ray powder diffraction, infra-red and ultra-violet/visible spectroscopy experiments were carried out on both series of samples. X-Ray diffraction data showed that single phase orthorhombic ferrites were produced. The ferrites showed a systematic decrease in lattice parameters and unit cell volume with chromium content (*e.g.* for series 1: $x=0$, $V=242.4$ Å^3; $x=1$, $V=234.0$ Å^3). ^{57}Fe Mössbauer spectroscopy indicated that at low Cr concentration ($x=0.1$ and 0.25) more than 96% of the Fe atoms experienced a perturbative disruption to their interatomic exchange interactions, consistent with the random distribution of Cr^{3+} ions on the B sublattice. The remaining 4% or less of Fe atoms were observed in a paramagnetic state, indicating a small degree of inhomogeneous Cr clustering in the lattice. The room temperature exchange interaction percolation limit for Cr substitution of the Fe lattice was found to lie between $x=0.4$ and 0.55, and the Mössbauer spectra for the $x \geqslant 0.55$ samples showed paramagnetic singlets. Room temperature magnetisation *versus* field curves showed hysteresis loops for $x \leqslant 0.7$ (series 1) and $x \leqslant 0.55$ (series 2), and anhysteretic curves for higher Cr contents. After an initial decrease with increasing Cr, the maximum magnetisations of the samples peaked at $x=0.25$ ($\sigma_{max}=2.1$ emu g^{-1}, series 1) and $x=0.4$ ($\sigma_{max}=1.7$ emu g^{-1}, series 2), before falling to near zero at higher concentrations. These features are consistent with a more homogeneous Cr substitution of the Fe sublattice in the series 2 samples, related to higher diffusion rates during the hotter combustion reactions achieved in the applied field SHS reactions. These results indicate that the SHS route is a potentially useful means of synthesising orthoferrites with desirable properties.

Introduction

Rare earth orthoferrites $RFeO_3$ (R = Y or lanthanide) and orthochromites $RCrO_3$ constitute a family of Dzyaloshinsky-interaction antiferromagnets which exhibit an unusual variety of magnetic properties and structural changes.[1–3] From a technological viewpoint these compounds have been proposed for use in resonance-based devices such as logic and memory elements, and as lasers and light modulators in optical applications.[4,5] These materials are also known to be catalytically active for the complex oxidation of hydrocarbons and as combustion catalysts, as well as being used as sensors and as solid electrolytes.[6–8]

Rare earth orthoferrites contain only trivalent metals in the structure, making them attractive systems for investigations of isovalent substitutions. In particular, the replacement of Fe^{3+} by Cr^{3+} and its effect on structural, magnetic and other properties have been reported by several groups.[9–13] In the lanthanum orthoferrites, partial replacement of Fe by Cr leads to a reduction in the Néel temperature from 750 K in $LaFeO_3$ through to 280 K in $LaCrO_3$. A Vegards law reduction in cell parameters is also observed on successive replacement of iron by chromium: $a=5.565$ to 5.485 Å, $b=5.565$ to 5.510 Å, and $c=7.850$ to 7.760 Å.[11,12]

Traditional synthesis routes to chromium substituted lanthanum orthoferrites involve a two step procedure: firstly the heating of lanthanum, iron and chromium(III) oxides in air for 24 h at 1000 °C; followed by the sintering of the reground samples in an oxygen atmosphere at 1400 °C for 24 h. Here we present a new method of synthesising chromium substituted lanthanum orthoferrites by self-propagating high-temperature synthesis (SHS). The SHS reaction is a fast exothermic solid state reaction that produces easily sinterable near-to-final products in seconds by promotion of a synthesis wave through the material. The passage of the synthesis wave is driven by the exothermicity of the chemical reaction. In particular we report on some intriguing observations obtained on carrying out the reactions in the presence of an external magnetic field.

Experimental

All reagents were obtained from Aldrich Chemical Co. and used as supplied. All the manipulations, weighings and

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grindings were performed under a nitrogen atmosphere in a Saffron Scientific glove box. Zero field SHS experiments were carried out in air with preground powders on a ceramic boat. Applied field SHS reactions were carried out in air inside a quartz tube. The tube (inner diameter 15 mm) was placed within a Halbach cylinder magnet manufactured by Magnetic Solutions Ltd. The Halbach cylinder comprised eight NdFeB magnets arranged to provide a field of 1.1 T along the cylinder's 10 cm length (<2% deviation in field along the axis). Sintering was carried out on reground powders in a Carbolite rapid heating furnace with heating and cooling rates of 10 °C min^{-1}. Powder X-ray diffraction (XRD) measurements were performed on a Philips X-pert diffractometer using filtered Cu-Kα radiation in the reflection mode ($\lambda = 1.5046$ Å). Lattice parameters were determined by using the program Unit Cell. Scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX) measurements were carried out on a Hitachi S4000. Vibrating sample magnetometry (VSM) was performed on an EG&G Princeton Applied Research M4500 magnetometer at room temperature in applied fields of up to 13 kOe. ^{57}Fe Mössbauer spectra were recorded with a Wissel MR-260 constant acceleration spectrometer with a triangular drive waveform. Spectra were folded to remove baseline curvature and were calibrated relative to α-iron at room temperature. FT-IR spectra were obtained on a Nicholet 205 using pressed KBr discs.

Sample preparation

SHS reactions were performed on various starting mixtures of La_2O_3, Fe_2O_3, Fe, Cr, Cr_2O_3 and $NaClO_4$. The molar ratio of each reagent was chosen to conform to the stoichiometry and oxygen content of the product. Sodium perchlorate was used as an internal oxidising agent for the combustion process. On decomposition, perchlorate produces oxygen which oxidises the Fe and Cr metal fuel sources for the reaction. Sodium chloride is also produced on decomposition of the perchlorate. This provides additional energy for the reaction and also acts as a wetting agent that helps to ensure passage of the propagation wave through the solid. The sodium chloride co-product is readily removed after the reaction by washing the as-formed powder with water. Different reagent mixtures were used across the $LaFe_{1-x}Cr_xO_3$ series. For the reactions with $x \leqslant 0.4$, Fe was used as a fuel source, and Cr_2O_3 as a source of Cr:

$$La_2O_3 + 2(1-x)Fe + xCr_2O_3 + 0.75(1-x)NaClO_4 \rightarrow 2LaFe_{1-x}Cr_xO_3 + 0.75(1-x)NaCl$$

For higher levels of Cr substitution ($x \geqslant 0.55$), Cr was used as a fuel source, and Fe_2O_3 as a source of Fe:

$$La_2O_3 + 2xCr + (1-x)Fe_2O_3 + 0.75xNaClO_4 \rightarrow 2LaFe_{1-x}Cr_xO_3 + 0.75xNaCl$$

All the reactions were carried out in air. The limiting stage of the reactions is the oxidation of the metal powders. In all the reactions the product was a brown or green-brown powder. The reaction scale in all cases was based on 10 g of reagent.

Two different series of samples were prepared: series 1 – zero field SHS followed by sintering at 1400 °C for 36 h; and series 2 – SHS in an applied field of 1.1 T followed by sintering at 1400 °C for 36 h. In both series the sintering was stopped after 12 h, the sample cooled to room temperature and reground, and the sintering resumed for the remaining 24 h.

Caution

SHS reactions produce rapid heating and cooling. Hot material can be ejected from the reaction site during the passage of the synthesis wave. On all new systems the reaction scale should be kept to a minimum (typically less than 1 g of total reagents). Sodium perchlorate is a vigorous oxidising agent and can ignite when ground with metal powders.

Results

The reactions proceeded from a point source of ignition by means of a yellow coloured synthesis wave at *ca.* 1100 °C. The velocity of propagation was approximately 4 mm s^{-1}. The reaction was driven by the oxidation of chromium and iron metals. The sodium perchlorate acts as an internal oxidising agent, providing further reaction energy on decomposition and providing sodium chloride that acts as a wetting agent in the process to help the diffusion of ions at the reaction front. The lanthanum oxide provides a source of lanthanum for the final product and also acts as a moderator absorbing some of the reaction enthalpy.

The product as formed from the reactions was predominantly the required chromium substituted lanthanide orthoferrite. However, the as-formed product did contain some unreacted starting materials as well as metal oxides and sodium chloride. Trituration of the product with water removed all of the sodium chloride (to below EDAX detection limits). Sintering the triturated powder at 1400 °C for 36 h produced single phase $LaFe_{1-x}Cr_xO_3$.

X-Ray powder diffraction data showed that single-phase orthorhombic perovskite structures were produced for both series of sintered powders $LaFe_{1-x}Cr_xO_3$. Representative diffractograms are shown in Fig. 1. The diffraction patterns indexed well and agreed with literature measurements for conventionally prepared materials.[11,12] Notably the unit cell volume, *a*, *b* and *c* parameters all decreased with chromium content, as indicated in Table 1.

FT-IR spectra for both series 1 and series 2 samples show predominantly a single broad band at 550–600 cm^{-1}. The band shifts almost linearly from 550 cm^{-1} for $LaFeO_3$ to 600 cm^{-1} for $LaCrO_3$. SEM/EDAX and electron probe measurements of both series of sintered samples showed that the materials were homogeneous with the expected La : Fe : Cr elemental ratios. SEM showed micron sized agglomerates of crystallites. UV spectra of both series of sintered samples were recorded in the range 200–1000 nm. UV spectra for the series 2 samples showed

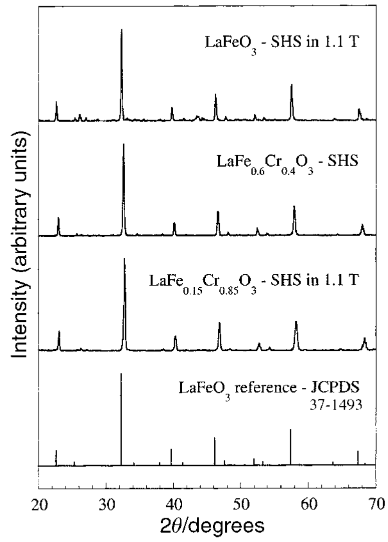

Fig. 1 X-Ray powder diffraction patterns for: $LaFeO_3$ obtained *via* the SHS reaction route undertaken in the presence of an external applied field of 1.1 T; $LaFe_{0.6}Cr_{0.4}O_3$ obtained *via* SHS in zero field; $LaFe_{0.15}Cr_{0.85}O_3$ obtained *via* SHS in a field of 1.1 T; and the standard reference pattern for $LaFeO_3$. All data are for sintered material (1400 °C, 36 h).

Table 1 Lattice parameters for two series of $LaFe_{1-x}Cr_xO_3$ orthoferrites obtained following the SHS reaction of Fe, Cr, Fe_2O_3, La_2O_3, Cr_2O_3 and $NaClO_4$ either in zero field (denoted Series 1) or in an applied field of 1.1 T (denoted Series 2). In both cases sintering at 1400 °C for 36 h with intermediate grinding operations followed the initial SHS preparation. The lattice parameters and unit cell volumes listed were obtained by X-ray analysis at room temperature

	Series 1				Series 2			
x	a/Å(±0.004)	b/Å(±0.004)	c/Å(±0.004)	V/Å^3(±0.5)	a/Å(±0.004)	b/Å(±0.004)	c/Å(±0.004)	V/Å^3(±0.5)
0	5.560	5.551	7.854	242.4	5.550	5.543	7.843	241.3
0.10	5.552	5.545	7.839	241.3	5.548	5.539	7.836	240.8
0.25	5.543	5.530	7.833	240.1	5.540	5.525	7.830	239.7
0.40	5.530	5.522	7.810	238.5	5.528	5.517	7.802	238.0
0.55	5.525	5.511	7.801	237.5	5.520	5.509	7.795	237.0
0.70	5.512	5.504	7.789	236.3	5.510	5.502	7.785	236.0
0.85	5.508	5.492	7.773	235.1	5.506	5.490	7.770	234.9
1.00	5.502	5.481	7.761	234.0	5.500	5.479	7.758	233.8

a decrease in percentage absorption from 1.55% at $x=0$ to 0.65% at $x=0.9$.

Mössbauer spectra were recorded at room temperature for all the samples from $LaFeO_3$ to $LaFe_{0.45}Cr_{0.55}O_3$ (see Fig. 2).

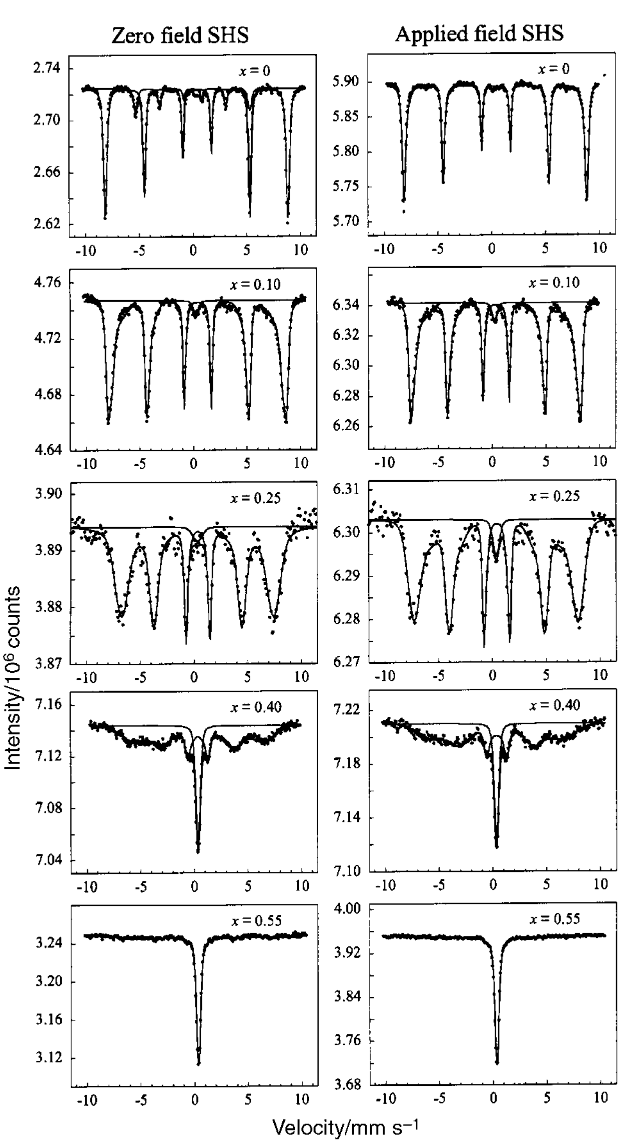

Fig. 2 Room temperature Mössbauer spectra for $LaFe_{1-x}Cr_xO_3$ ($x=0$, 0.1, 0.25, 0.40, 0.55) derived from SHS reactions in zero field and in an external magnetic field of 1.1 T. With the exception of the zero field $x=0$ sample, all the data are for samples obtained after post-SHS sintering at 1400 °C for 36 h. The zero field $x=0$ sample shown is a post-SHS, unsintered material, which contains a small amount of unreacted α-Fe reagent, corresponding to approximately 15% of the total spectral area.

These spectra were least squares fitted using combinations of Voigtian profile singlets and sextets to model distributions in the local environments of the Fe atoms.[14] Selected parameters from these fits are given in Table 2. The data show that in both series of samples the incorporation of increasing amounts of Cr into the orthoferrite lattice results in the growth of a paramagnetic singlet component, and the accompanying reduction in the mean hyperfine field and increased broadening of a magnetic sextet component. Differences between the two series are minor, and relate primarily to the relative areas of the singlet and sextet components, and the mean hyperfine fields of the sextet component (see Table 2). None of the sintered samples show any signs of unreacted reagents. In contrast, a Mössbauer spectrum recorded for a sample of the unsintered $x=0$ zero field SHS product showed a second magnetic sextet with parameters identifying it as α-iron (Fig. 2), indicating that some unreacted reagent persisted.

Magnetisation *versus* field curves were recorded at room temperature in applied fields of up to 13 kOe for all the sintered samples. Representative curves are shown in Fig. 3, and extracted data – the maximum magnetisation $\sigma_{\max}$, remanent magnetisation σ_r and coercivity H_c – are given in Table 3. For the series 1 samples with $x \leqslant 0.7$, and for the series 2 samples with $x \leqslant 0.55$, magnetic hysteresis was observed, indicating the existence of weak ferromagnetism. At higher Cr concentrations, in both series, anhysteretic curves were observed. Systematic variations in the maximum magnetisations were observed, as shown in Fig. 4. In both series of samples $\sigma_{\max}$ first decreased as Cr was added, then increased to a maximum (at $x=0.25$ for series 1 and $x=0.4$ for series 2) before falling to almost zero at the highest Cr concentrations.

Discussion

The variation in unit cell size of $LaFe_{1-x}Cr_xO_3$ with increasing chromium content can be attributed to the smaller ionic radii of six-fold co-ordinated Cr^{3+} ions (0.64 Å) compared to those of six-fold Fe^{3+} ions (0.67 Å). All the samples gave X-ray patterns characteristic of orthorhombic perovskite. The lattice parameters a, b and c and cell volumes V showed a quasi-linear decrease with Cr content, the slight non-linearity possibly being due to a changing magnetostrictive effect as a function of Cr concentration. The overall percentage decrease in cell size for the series 1 and 2 parameters is different: in the range $0 \leqslant x \leqslant 1$ for series 1 the reductions in a, b, c and V were 1.04, 1.26, 1.18 and 3.45% respectively; compared to 0.90, 1.15, 1.08 and 3.11% for series 2. Although these differences are small, similar differences between the lattice parameters of materials synthesised *via* SHS in zero field and in an applied field have been noted in other systems, including $MgFe_2O_4$,[15] $LiFe_5O_8$ [16] and $BaFe_{12}O_{19}$,[16,17] implying that this is a significant effect. The origin of this effect is the subject of on-going investigation. However, it is notable that since these materials are sintered at

Table 2 Room temperature Mössbauer parameters for $LaFe_{1-x}Cr_xO_3$ ferrites, produced by SHS in zero field (Series 1) or in an applied magnetic field 1.1 T (Series 2), followed by sintering at 1400 °C for 36 h with intermediate grinding. The spectra were fitted using Voigtian profile singlet and/or sextet components to model the distributions in local Fe environments resulting from the substitution of Cr^{3+} ions onto the Fe^{3+} lattice. The parameters listed are the isomer shift δ and percentage spectral area $A_{singlet}$ of the singlet component, and the mean absolute hyperfine field $\langle|B_{hf}|\rangle$ and standard deviation $\sigma_{|Bhf|}$ of the distribution of hyperfine fields incorporated in the sextet component

	Series 1				Series 2			
x	δ/mm s^{-1}	$A_{singlet}$ (%)	$\langle\lvert B_{hf}\rvert\rangle$/kOe	$\sigma_{\lvert Bhf\rvert}$/kOe	δ/mm s^{-1}	$A_{singlet}$ (%)	$\langle\lvert B_{hf}\rvert\rangle$/kOe	$\sigma_{\lvert Bhf\rvert}$/kOe
0	—	0	527(3)^a	9(1)^a	—	0	523(5)	13(3)
0.10	0.23(7)	1.9(4)	493(10)	34(5)	0.26(6)	2.5(5)	468(12)	34(8)
0.25	0.36^b	2.4(15)	427(20)	72(9)	0.36(8)	4(1)	447(10)	62(7)
0.40	0.35(1)	23(2)	317(35)	117(30)	0.35(1)	22(2)	326(35)	119(25)
0.55	0.36(1)	100	—	—	0.36(1)	100	—	—

^{a}Sample prepared by SHS only, without sintering. A second sextet due to incompletely reacted α-Fe was also fitted in this spectrum. ^{b}Parameter not allowed to vary during fit.

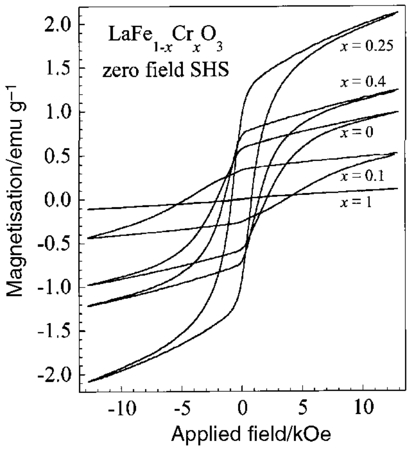

Fig. 3 Representative room temperature magnetisation curves for $LaFe_{1-x}Cr_xO_3$ samples derived from SHS reactions in zero field, followed by sintering at 1400 °C for 36 h.

well above their Curie temperatures, it cannot be a simple magnetostrictive effect.

The room temperature Mössbauer spectra obtained from the sintered SHS products are consistent with a slightly inhomogeneous substitution of the B sublattice iron atoms with chromium. The spectra of the $LaFeO_3$ samples showed a single Fe(III) sextet component with sharp lines, confirming that all the iron atoms are in equivalent crystallographic positions. On the introduction of chromium into the lattice (i) a second subcomponent spectrum, a singlet, appears, and (ii) the sextet lines become broader and encompass a smaller velocity range between the outermost peaks. These features correspond to (i) an increasing fraction of the Fe^{3+} ions encountering severe disruption to their interatomic magnetic exchange interactions, leading to their adopting a paramagnetic state;† and (ii) the remaining Fe^{3+} ions encountering an increasing degree of perturbative disruption to their local environments, leading to an increasingly broad distribution of magnetic hyperfine fields at the Fe nuclei, coupled with a reduction in the mean hyperfine fields. The measured reduction in hyperfine field varies smoothly and roughly linearly with chromium content in the range $0 \leqslant x \leqslant 0.40$. For the $x = 0.55$ samples a paramagnetic singlet pattern dominates the Mössbauer spectra, with only a small amount (relative area ~2%) of magnetic sextet absorption being visible in the wings of the series 1 sample's spectrum, and none at all in the series 2 sample's spectrum. These observations are consistent with the magnetic ordering temperatures of the samples decreasing with increasing Cr substitution: approaching room temperature for the $x = 0.55$ series 1 sample, and falling below room temperature for the $x = 0.55$ series 2 sample.

Similar features have been observed in previous Mössbauer investigations of substituted spinels[18] and also in other substituted ferrites.[19] At low Cr substitution levels they may be attributed to inhomogeneous substitution, leading to some of the Fe atoms becoming isolated from the other exchange-coupled Fe atoms. This results in paramagnetic behaviour, which gives rise to the singlet. The degree of inhomogeneity can be estimated by considering the relative spectral area in the singlet component. In the $x = 0.10$ and 0.25 samples the singlet area is of order 2–4%, indicating that the chromium substitution is largely homogeneous, with $\geqslant$96% of the Fe atoms experiencing only the perturbative disruption to their exchange interactions that would be expected for a totally random substitution of Cr. At higher Cr concentrations the paramagnetic component becomes associated with the Fe lattice as a whole. The singlet area in the $x = 0.40$ samples is of the order 23%, while it is of the order 100% for the $x = 0.55$ samples. This rapid rise in the spectral area implies that the range of compositions $0.40 \leqslant x \leqslant 0.55$ covers the room temperature percolation limit for Fe–Fe exchange interactions in the lattice.

The magnetisation data reveal further information on the effect of Cr substitution on the magnetism of the orthoferrite lattice. The weak ferromagnetism in the $x = 0$ samples arises from spin canting induced by the Dzyaloshinsky interaction, and is apparent in the hysteresis loop, which has a sizeable

Table 3 Room temperature magnetic properties for $LaFe_{1-x}Cr_xO_3$ ferrites, produced by SHS in zero field (Series 1) or in an applied magnetic field of 1.1 T (Series 2), followed by sintering at 1400 °C for 36 h with intermediate grinding operations. The parameters listed are the maximum magnetisation σ_{max} ($\pm$0.01 emu g^{-1}) recorded in an external field of 13 kOe, the remanent magnetisation σ_r ($\pm$0.01 emu g^{-1}) and the coercive force H_c ($\pm$10 Oe)

	Series 1			Series 2		
x	σ_{max}	σ_r	H_c	σ_{max}	σ_r	H_c
0	0.99	0.58	2100	0.75	0.52	4440
0.10	0.52	0.34	4670	0.73	0.50	4480
0.25	2.13	0.97	810	0.35	0.17	4180
0.40	1.24	0.73	1470	1.72	0.78	960
0.55	0.86	0.50	1290	0.25	0.02	600
0.70	0.71	0.37	1960	0.17	0.01	210
0.85	0.24	0.02	170	0.15	0.01	160
1.00	0.11	0.01	160	0.13	0.01	230

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†We note that an alternative hypothesis, applicable for the $x = 0.1$ and 0.25 samples, is that the singlet could be due to a minor impurity phase that had gone undetected in the X-ray diffraction data. However, this is unlikely, since the most plausible iron-containing impurities would be either unreacted iron metal or an iron oxide such as hematite, either of which would give rise to a magnetically split sextet or, in the case of fine particle (superparamagnetic) oxides, a doublet with a quadrupole splitting of 0.6 mm s^{-1}, rather than a singlet.

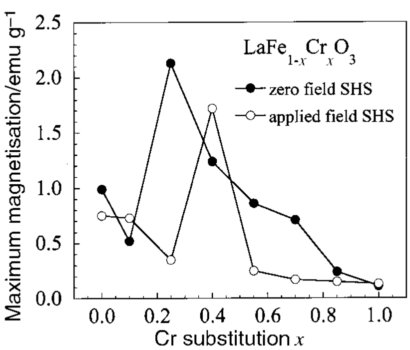

Fig. 4 Variation with composition of the maximum magnetisation σ_{max} for two series of $LaFe_{1-x}Cr_xO_3$ samples derived from SHS reactions in zero field and in an external magnetic field of 1.1 T, followed by sintering at 1400 °C for 36 h. The data were obtained at room temperature in an applied field of 13 kOe.

coercivity ($H_c \sim 2$ kOe in series 1) and a small magnetisation ($\sigma_{max} \sim 1.0$ emu g^{-1} in series 1). Adding a small amount of Cr disrupts the Fe–Fe exchange interactions, leading to reduced atomic moment magnitudes, and a reduced magnetisation. Further addition of Cr breaks up the exchange interactions still further, and may lead to the formation of an inhomogeneous distribution of spin clusters on the lattice that may more freely orientate in response to an applied magnetic field, and therefore deliver an enhanced magnetisation. Increasing the Cr content further leads to increasing disruption of the exchange interactions, leading to a paramagnetic state at the highest Cr concentration. These various regimes of behaviour are evident in the σ_{max} data in Fig. 4, where it is also apparent that there are clear differences between the magnetic properties of the series 1 and series 2 samples. The series 2 (applied field SHS) samples attain the paramagnetic states at lower Cr concentrations than do the series 1 (zero field SHS) samples, while they attain the spin-clustering magnetisation enhancement state at a higher concentration. Both of these observations are consistent with the hypothesis that the Cr substitution into the Fe sublattice is more homogeneous in the series 2 samples than it is in the series 1 samples. Greater heterogeneity (as in series 1) would promote spin clustering at lower Cr contents; greater homogeneity (as in series 2) would promote the early establishment of a paramagnetic state. The origin of such an effect could lie in a higher SHS combustion temperature in the applied field case compared to the zero field case. Although the combustion temperatures of the lanthanum orthoferrite reactions were not measured, previous works on other ferrite systems have consistently reported higher reaction temperatures in the applied field reactions.[15–18] Higher reaction temperatures could promote higher rates of diffusion, leading to improved cationic distribution homogeneities.

Lastly, we note that the magnetisation data differ somewhat from that reported for samples made by conventional synthesis routes. For example, literature values for the remanence in $x = 0.55$ and $x = 0.70$ samples are 0.50 emu g^{-1} and close to zero, respectively.[11,12] In each case the series 1 and 2 SHS datapoints bracket these values. In light of the preceding discussion, this implies that the conventional synthesis route may lead to products that are more homogeneous than those obtained by zero field SHS, and less homogeneous than those obtained by applied field SHS.

Conclusions

We have shown that a full range of single-phase pure and chromium substituted lanthanum orthoferrites $LaFe_{1-x}Cr_xO_3$ ($0 \leqslant x \leqslant 1$) can be synthesised in air *via* the SHS route in which a combustion reaction is initiated between lanthanum(III) oxide, iron(III) oxide, chromium(III) oxide and iron (or chromium) metal powders, followed by sintering at 1400 °C for 36 h with intermediate grinding. X-Ray diffraction data showed a systematic decrease in lattice parameters and unit cell volume with chromium content (*e.g.* for series 1: $x = 0$, $V = 242.4$ Å^3; $x = 1$, $V = 234.0$ Å^3).

^{57}Fe Mössbauer spectroscopy indicated that at low Cr concentration ($x = 0.1$ and 0.25) more than 96% of the Fe atoms experienced a perturbative disruption to their interatomic exchange interactions, consistent with the random distribution of Cr^{3+} ions on the B sublattice. The remaining 4% or less of Fe atoms were observed in a paramagnetic state, indicating a small degree of inhomogeneous Cr clustering in the lattice. The exchange percolation limit for Cr substitution of the Fe lattice was found to lie between $x = 0.4$ and 0.55, with the Mössbauer spectra for the $x \geqslant 0.55$ samples all being paramagnetic singlets.

Some differences were observed in both magnetic and structural properties between samples prepared *via* SHS in zero field and SHS in an applied field of 1.1 T. Although the precise details of the origin of this effect are the subject of continuing investigations, the variations in magnetic properties in particular may plausibly be associated with differences in the homogeneity of the Cr substitution onto the Fe sublattice. This intriguing result shows that in addition to being a convenient route to the zero field synthesis of lanthanum orthoferrites, the SHS process, when conducted in the presence of an external field, may also be a potentially useful means of synthesising orthoferrites with novel and desirable magnetic properties.

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