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Authors

Volodchenkov, AD

Kodera, Y

Garay, JE

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Synthesis of strontium ferrite/iron oxide exchange coupled nano-powders with improved energy product for rare earth free permanent magnet applications

A. D. Volodchenkov,^{ab} Y. Koderá^{*ab} and J. E. Garay^{*abc}

We present a simple, scalable synthesis route for producing exchange coupled soft/hard magnetic composite powder that outperforms pure soft and hard phase constituents. Importantly, the composites are iron oxide based ($\text{SrFe}_{12}\text{O}_{19}$ and Fe_3O_4) and contain no rare earth or precious metals. The two step synthesis process consists of first precipitating an iron oxide/hydroxide precursor directly on top of $\text{SrFe}_{12}\text{O}_{19}$ nano-flakes, ensuring a very fine degree of mixing between the hard and the soft magnetic phases. The second step involves the reduction of the precursor to create the appropriate soft magnetic phase and create the intimate interface necessary for exchange coupling. We establish a clear processing window; at temperatures below this window the desired soft phase is not produced, while the use of higher temperatures results in deleterious reaction at the soft/hard phase interfaces, causing an improper ratio of soft to hard phases. Improvements in M_r , M_s , and $(\text{BH})_{\text{max}}$ are 42%, 29% and 37%, respectively, in the $\text{SrFe}_{12}\text{O}_{19}/\text{Fe}_3\text{O}_4$ composite compared to the pure hard phase ($\text{SrFe}_{12}\text{O}_{19}$). We provide evidence of coupling (exchange spring behavior) with hysteresis curves, first order reversal curve (FORC) analysis and recoil measurements.

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Introduction and background

Permanent magnets (PMs) are essential to an amazing variety of current and future devices, causing widespread interest in improving PM performance. Magnets with high rare earth (RE) contents such as Nd–Fe–B (typically with composition $\text{Nd}_2\text{Fe}_{14}\text{B}$) and Sm–Co (typically SmCo_5) are currently the state of the art PMs. One approach to increasing the PM performance is the exchange spring concept which has been predicted to yield huge gains in the energy product, $(\text{BH})_{\text{max}}$ (figure of merit for PM performance).¹ This promise has inspired successful pioneering research in RE based exchanged-coupled PMs^{2–6} as well as in Fe–Pt based PMs.^{7,8} For example Lyubina *et al.*⁶ showed evidence of exchange coupling in Fe–Pt powders while Liu and Davies⁸ showed exchange in RE–iron melt spun alloys.

A natural extension of the exchange spring concept is to replace expensive and threatened magnetic phases (such as RE or Pt based materials) with much more abundant and accessible

materials. Along these lines, Roy *et al.*⁹ were able to synthesize all ferrite materials with exchange spring behavior. In this work we chose strontium ferrite ($\text{SrFe}_{12}\text{O}_{19}$) as a hard phase and Fe_3O_4 as a soft phase. $\text{SrFe}_{12}\text{O}_{19}$, henceforth to be referred to as SFO, is mostly Fe and O which are two of the most abundant elements on earth. This makes SFO a popular PM material in a host of consumer devices.^{1,10} While the coercivity of SFO cannot compete with that of RE based hard magnets, the complete elimination of REs and expensive elements is an enticing compromise. The soft phase is composed of only Fe and O and thus is extremely inexpensive and abundant. Cubic Fe_3O_4 has a saturation magnetization of 84 emu g^{-1} ,² higher than pure SFO (42 emu g^{-1}) which can potentially lead to an exchange coupled SFO/ Fe_3O_4 composite that outperforms pure SFO.

In addition to using earth abundant, low cost elements, PM material implementation would benefit tremendously from low cost, scalable synthesis procedures. A particular beneficiary would be PMs for motors and generators since kilogram quantities are necessary for these applications.⁷ Exchange coupling relies heavily on a high interaction area between the hard phase and the soft phase, requiring the grains of soft and hard materials to be in the sub-micrometer/nanometer range and well intermixed.³ The combination of nano-grains, good mixing, as well as clean interfaces makes the synthesis of exchange coupled PMs using a scalable and economical synthesis procedure challenging.

^a Advanced Materials Processing and Synthesis (AMPS) Laboratory, Mechanical Engineering Department, University of California, Riverside, USA.
E-mail: ykoderá@engr.ucr.edu

^b Materials Science and Engineering Program, Mechanical Engineering Department, University of California, Riverside, USA

^c Materials Science and Engineering Program, Mechanical and Aeronautical Engineering Department, University of California, San Diego, USA

Fig. 1 Schematic of hard/soft composite synthesis.

Among the many different approaches to synthesize powder, the homogeneous precipitation (HP) method is one of the most common approaches used in inorganic chemistry for laboratory and industrial scales.^{11,12} HP generally provides good morphology and crystal phase control without the need for extreme conditions/systems, such as rapid heating/cooling, high vacuum, high pressure, *etc.* There have been previous successful soft chemistry routes^{13,14} for obtaining exchange coupled particles, although these pioneering cases did not always lead to improved $(BH)_{\max}$ without the use of non-earth abundant materials and extreme conditions. Our concept of synthesizing composite PMs is a twostep process, shown schematically in Fig. 1. First we use HP to precipitate a Fe–O/Fe–O–H precursor directly on top of SFO nano-flakes, ensuring a very fine degree of mixing between the hard and the soft magnetic phases. We then use a second step that serves to reduce the precursor to create the proper soft magnetic phase and create the intimate interface necessary for coupling. The result is a simple, inexpensive synthesis route for exchange coupled PM composite powder that outperforms pure SFO.

Experimental procedure

a. Material synthesis

Precipitation by decomposition of urea was chosen as the method of depositing Fe oxide/hydroxide (Fe–O/Fe–O–H as the precursor of the soft phase) onto SFO powder (SrFe₁₂O₁₉, Nanostructured & Amorphous Materials Inc.). The SFO powder consists of high aspect ratio flake like particles with an average diameter of 1.12 μm and a thickness of 0.16 μm . As starting materials for Fe oxide/hydroxide precipitation, 28.7 mmol of Fe(NO₃)₃ (Sigma Aldrich >98%) and 167 mmol of CO(NH₂)₂ (urea; Sigma Aldrich >99.5%) were mixed into 150 ml of H₂O. The mixture was then titrated into a slurry of 1.58 mmol of SFO and 50 ml of H₂O. The temperature was maintained at 90 °C for 2 hours. The resulting composite powder was cooled quickly to prevent further particle growth.

In order to understand the Fe–O/Fe–O–H precipitation process (phase and morphology development during the process) we also did experiments without the SFO (soft phase only) in which no titration is used. The same amount of Fe(NO₃)₃ and 167 mmol of urea was mixed into 150 ml of H₂O and held at 90 °C for 2 hours. The resulting homogeneous precipitation creates nano-scale particles of the soft magnetic phase precursor.

In both the composite and soft phase cases, the resulting particles were centrifuged, washed with ultra-high pure water and centrifuged again. The powder and liquid was separated

by decantation. The powder was dried at 80 °C in a vacuum furnace for 24 hours to ensure no moisture remains after which the dried agglomerates are broken by mortar and pestle. The powders were then treated in a tube furnace under forming gas (5% H₂, 95% N₂) at temperatures ranging from 300 °C to 500 °C with 1 hour ramp and no hold time. The resulting powder was handled in an Argon atmosphere to avoid oxidation.

The yield of Fe–O precipitation was obtained by the gravimetric analysis based method. The liquid collected from decantation was dried and calcined at 800 °C for 6 h in an air atmosphere. The residue remaining after calcination was the α -Fe₂O₃ single phase which was confirmed by X-ray diffraction analysis. The amount of α -Fe₂O₃ was used to calculate the yield of the precipitation process.

b. Structural and microstructural characterization

The phase composition was characterized by X-ray diffraction (XRD) (PANalytical Empyrean Diffractometer with a Cu K α X-ray source $\lambda_{K\alpha1} = 1.54056 \text{ \AA}$ $\lambda_{K\alpha2} = 1.54440 \text{ \AA}$ using a 0.01313° step size). In order to provide a simplified estimate of the phase composition ratio, the XRD peak intensity ratio was calculated by taking the highest intensity peak of one phase and dividing it by the sum of the highest intensity peaks of all detectable phases and multiplying by 100. The particle morphology was characterized by Scanning Electron Microscopy (SEM) (Philips XL30).

c. Magnetic measurements

Magnetic properties were measured using a Vibrating Sample Magnetometer (VSM) (Lakeshore 7400 Series) at room temperature. Hysteresis loop measurements using field values of up to 1.7 T were obtained in order mass normalized magnetization, σ [emu g^{−1}] vs. applied field, H [Oe]. We refer to these measurements as customary hysteresis loops. Coercivity, H_c [Oe], remanent magnetization M_r [emu g^{−1}] and saturation magnetization M_s [emu g^{−1}] was extracted from the σ vs. H hysteresis curves. While calculating M_s , the non-saturating slope (due to SFO and Fe₃O₄ being ferrimagnetic) was subtracted. The energy product, $(BH)_{\max}$ [MGOe], was calculated assuming full density of SFO.

First order reversal curve (FORC) measurements were done by ramping the field to 0.6 T then decreasing the magnetic field to a reversal field with a value of H_a and ramping back up to 0.6 T through field values, H_b with a step size of 200 Oe. Magnetization as a function of H_a and H_b , $M(H_a, H_b)$, is recorded. This procedure was repeated in order to measure a collection of first order reversal curves for reversal fields in 200 Oe intervals from 5800 Oe to −6000 Oe. FORC distribution, ρ , is calculated using the relation:⁵

$$\rho(H_a, H_b) = -\frac{\partial^2 M(H_a, H_b)}{\partial H_a \partial H_b} \quad (1)$$

FORCinel was used to calculate the FORC distribution and plot it, traditionally, as H_c vs. H_u where $H_c = (H_b - H_a)/2$ and $H_u = (H_a + H_b)/2$.¹⁵

Recoil loop measurements were done by first ramping the magnetic field to 1.7 T in order to bring the sample to saturation (ignoring the non-saturating component due to SFO and Fe₃O₄

being ferrimagnetic). A reversal field, H_a , was applied, removed (field taken to 0 Oe) and reapplied (field taken back to H_a). H_a values were varied from 100 Oe to 1400 Oe in 100 Oe increments. Measurements of magnetization, σ , were taken from H_a to 0 Oe, forming the recoil magnetization curve, and likewise from 0 Oe back to H_a , forming the recoil demagnetization curve. The area between recoil magnetization and recoil demagnetization curves was calculated using numerical methods. Normalized recoil loop area was calculated by dividing the area between recoil magnetization and recoil demagnetization curves by one half of the total area of the sample's customary hysteresis loop area (also calculated using numerical methods). M_{recoil} is the value of magnetization with a 0 Oe field applied following recoil magnetization from H_a to 0 Oe. The recoil remanence ratio M_{recoil}/M_r was calculated by taking the M_{recoil} values and dividing it by the magnetic remanence M_r (from the customary loop obtained as described above).

Results and discussion

Synthesis of the soft magnet phase

We start by discussing the Fe-based soft magnet powders (Fe–O/Fe–O–H) *i.e.* materials without the hard SFO phase. Although many different approaches have been reported for synthesizing iron hydroxides/oxides,^{11,12,16} it is important to understand the details of the synthesis and reduction behavior of iron hydroxide/oxide under our experimental conditions in order to achieve our goal of obtaining soft–hard composites with controlled properties. The precursor was synthesized through precipitation by thermal decomposition of urea in iron nitrate solution.^{12,17} There are several reports on the synthesis of iron hydroxide/oxide and oxide using iron salt and urea as reactants that produce fine nanoparticles and high yields.^{17–20} We chose iron nitrate and urea as reactants in this particular study because of the simplicity involved in the removal of ammonium nitrate (formed as byproduct) in the process.

Fig. 2 shows the XRD patterns of the as-precipitated powder from iron nitrate and urea solution heated at 90 °C. The XRD confirms that the product is a mixture of α -Fe₂O₃ and α -FeO(OH) and is of low crystallinity which agrees with previous results.²¹ The high background intensity at low angles suggests the presence of a low crystallinity/amorphous phase.

In order to achieve the desired soft phase (Fe₃O₄) the dried as-precipitated powder was then thermally treated in 95% N₂: 5% H₂ gas flow. The XRD patterns in Fig. 2 show the influence of the treating temperature on the reduction of the precipitated α -Fe₂O₃/ α -FeO(OH). Increasing the temperature causes the decomposition of α -FeO(OH) and the reduction of hexagonal Fe₂O₃ to cubic Fe₃O₄ and subsequently the reduction of Fe₃O₄ to metal α -Fe at higher temperatures. These observations agree with previous studies.^{22–25} FeO was not detected as the intermediate phase during the reduction process because the processing temperature was below 570 °C.²⁶ The phase evolution is more easily observed in Fig. 3 showing XRD peak intensity ratio *vs.* reduction temperature. At the processing temperature of 300 °C,

Fig. 2 X-ray diffraction patterns of the soft phase after precipitation as well as at reduction temperatures 300–500 °C.

Fig. 3 XRD peak intensity ratios at various reduction temperatures. The peak intensity ratio is the ratio of the most intense peak of a particular phase to the sum of the intensities of the most intense peaks of all identifiable phases. The most intense peaks for α -Fe, Fe₃O₄, α -Fe₂O₃ and α -FeO(OH) are from the (110), (311), (104) and (101) planes, respectively.

all of the as-precipitated phases are converted to Fe₃O₄. The metal α -Fe appears at 350 °C and its relative amount increases with temperature; however, it is not the major component until the reduction temperature is increased to 450 °C. At 500 °C, the reduction to form metal α -Fe was almost complete. This agrees well with previous work in which the complete reduction of fine Fe oxide powder was observed in H₂/Ar gas below 497 °C.²³

Fig. 4 shows the SEM micrographs of as-precipitated powder as well as heat treated ones. The as-precipitated particles exhibit morphologies with low aspect ratios and small grain sizes (tens of nm). Also the micrographs suggested the low degree of aggregation of particles. These morphological characteristics contribute to the ease of reduction.

The SEM micrograph of the sample reduced at 400 °C shows a significant change in surface roughness and evidence of grain growth. Considering this result and the reduction mechanism, we assume that about 70% of Fe₃O₄ remains as a core that is

Fig. 4 (a and b) SEM micrographs of as-precipitated soft phase powder. (c and d) SEM micrographs soft phase powder reduced at 400 °C.

surrounded by α -Fe (about 30%) as a shell at 400 °C. Despite the clear grain growth, these soft phases did remain at the nano-scale which is very important for obtaining an exchange coupled PM.

Synthesis of soft/hard magnet composites

Fig. 5 shows the XRD pattern of SFO powders after having undergone the precipitation of the soft phase precursor. Also shown in Fig. 5 are the XRD patterns of the soft/hard composite powders after reduction at various temperatures. The as-precipitated sample shows XRD patterns identical to as-received SFO (not shown here) and no significant peak from the precipitate except a small peak at 33 degrees corresponding to α -Fe₂O₃. This result suggests that there is no significant damage of SFO during the precipitation process. Fig. 6 shows XRD peak intensity ratio *vs.* reduction temperature. At 300 °C, the intensity of α -Fe₂O₃ peaks increases and the peaks of Fe₃O₄ appear. By contrast, the soft phase only results (Fig. 3) show the full conversion of the precursor to Fe₃O₄ at the same temperature (300 °C). In the case of the non-composite system, the entire surface of particles, except point contacts between particles, is exposed to the atmosphere; on

Fig. 5 X-ray diffraction patterns of the SFO-(Fe-O) composite after the precipitation procedure as well as at reduction temperatures 300–500 °C.

Fig. 6 XRD peak intensity ratios at varying reduction temperatures. The peak intensity ratio is the ratio of the most intense peak of a particular phase to the sum of the intensities of the most intense peaks of all identifiable phases. The most intense peaks for Fe₃O₄, α -Fe₂O₃ and SFO are from the (311), (104) and (107) planes, respectively.

the other hand, in the composite case (Fig. 6), α -Fe₂O₃ particles are precipitated on the SFO meaning at least one side of particles is not exposed to the atmosphere; this should slow down the reduction kinetics of Fe₃O₄ formation.

In addition to the reaction of the precipitated layer the decay of SFO was simultaneously observed by XRD. At 500 °C, the Fe₃O₄ peaks become more intense than the SFO peaks. This suggests that the reaction between the deposited layer and SFO takes place. This reaction is more intense at higher temperatures. Based on the results of the soft phase study shown in Fig. 3, the heat required to reduce iron oxide to metal α -Fe is enough to cause significant reaction between SFO and the soft magnet phase. In other words, too low a temperature produces SFO/ α -Fe₂O₃ composites instead of the desired SFO/Fe₃O₄ composites, while too high a temperature destroys the SFO phase, resulting in a composite with too much soft phase. These data clearly show that there is a limited processing temperature window that produces the desired phases.

Fig. 7 shows the SEM micrographs of samples of the as-received SFO powder as well as composite powders after the precipitation step and after the reduction step at various magnifications. The pure SFO (Fig. 7a–c) exhibits hexagonal facets which correspond to its crystal structure. When the precursor is precipitated on SFO, there are “clouds” of particles deposited on the surface and at the intersections of SFO grains (Fig. 7d–f). The higher magnification images show that the sizes of those particles are tens of nanometers. The XRD (Fig. 5) and SEM (Fig. 7) results confirm that we succeeded in synthesizing core/shell style (SFO/Fe₃O₄) nano-composite magnets. There have been other successful synthesis approaches to synthesize Sr or Ba hexaferrite/soft magnet composites,^{27–29} although previous work targeted different applications rather than permanent magnets. Multi-step methods like the one presented here are well suited for synthesizing core/shell structures¹⁴ that allow more control on the morphology and amount of individual

Fig. 7 (a–c) SEM micrographs of single phase SFO powder. (d–f) SEM micrographs of composite powder after the precipitation procedure. (g–i) SEM micrographs of composite powder after reduction at 400 °C.

phase (hard and soft) needed for producing coupled permanent magnets.

The calculated yield of the precipitated material (obtained from the gravimetric analysis method) was 62%. When precipitated the Fe based soft phase forms only Fe_3O_4 (e.g. the sample reduced at 400 °C), and the volume ratio of the hard/soft phase (SFO/ Fe_3O_4) is 55/45. We can use the measured yield and volume ratios to estimate the thickness of the Fe_3O_4 coating using the geometry and dimensions of the SFO/ Fe_3O_4 core/shell structure, which is calculated to be 43 nm on the surface of SFO assuming a hexagonal plate-like particle (regular hexagonal prism) as shown in Fig. 1. The dimensions used for this estimate are the average sizes measured for SFO (diameter of 1.12 μm and thickness of 0.16 μm).

After reducing the composites at 400 °C, there is no significant change in low magnification images and there are still relatively sharp corners/edges of SFO composite grains. This suggests that sintering and grain growth of SFO composites are not significant at this temperature. However, high magnification images (compare between Fig. 7a, d and g) reveal a clear change in the surface morphology of SFO composites. The SFO composite grains show agglomerated round shaped particles (tens of nanometers) with curved edges and many pores. This is caused by the reduction of the precursor and sintering of Fe_3O_4 during the reduction process. First, both decomposition and reduction reduce the number of atoms in the compound and create voids and pores. Then, sintering forms a neck and causes grain growth. Therefore, those voids and pores are segregated from the matrix to form the microstructure we see in Fig. 7i.

There is a clear contrast between the soft phase only and composite powders in the degree of grain growth. When the samples are treated at 400 °C, the soft magnet shows significant

grain growth, and on the other hand, the composite (soft phase on SFO) does not show such a drastic growth (see Fig. 4c and 7i). In order to have sufficient significant grain growth, two conditions are required: (1) there needs to be sufficient atomic mobility for grain growth. (2) There needs to be sufficient material to form coarse grains with larger volume. Since the soft phase results (Fig. 4) show significant grain growth there is sufficient thermal energy at 400 °C required for mobility indicating that there simply is not enough soft phase on the surface of SFO to form large grains in the composite case.

These structural and morphological characterization results confirm that we are successful in synthesizing SFO/ Fe_3O_4 nanocomposites by precipitation of the precursor on the SFO followed by a reduction process.

Magnetic properties

Magnetic saturation, M_s , taken from the measured hysteresis loops of soft phase powders is displayed in Fig. 8. Post precipitation, (0 °C in Fig. 8) the powder has very low M_s as expected for a powder composed of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeO(OH)}$ (see XRD results (Fig. 2)). Both $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeO(OH)}$ are antiferromagnetic. As we reduce the powder at 300 °C the hexagonal $\alpha\text{-Fe}_2\text{O}_3$ becomes mostly cubic Fe_3O_4 with a saturation magnetization of 93 emu g^{-1} . M_s increases further after 400 °C as the composition of $\alpha\text{-Fe}$ increases and cubic Fe_3O_4 decreases. After reduction at 500 °C the powder has a very high $M_s = 147 \text{ emu g}^{-1}$ as expected for a powder that is mostly $\alpha\text{-Fe}$.

The magnetic properties of the as received SFO and composite powder are displayed in Fig. 9. The single phase SFO powder has coercivity H_c , remanent magnetization M_r , saturation magnetization M_s , and energy product $(\text{BH})_{\text{max}}$ values of 967 Oe, 18.3 emu g^{-1} , 42 emu g^{-1} and 0.165 MGOe. The $(\text{BH})_{\text{max}}$ values were those

Fig. 8 Saturation magnetization of the soft phase at various reduction temperatures.

Fig. 9 SFO/(Fe-O) composite magnetic properties (coercivity, remanent magnetization, saturation magnetization, and energy product).

calculated assuming a full density of 5.1 g cm^{-3} for SFO.³⁰ SFO has hexagonal symmetry with relatively high magnetocrystalline anisotropy. These values are in the range of expected values for SFO and provide benchmark values *i.e.* the main goal of the study is to achieve a composite PM with $(BH)_{\text{max}}$ higher than 0.165. It should be noted that it is possible to produce SFO magnets with higher $(BH)_{\text{max}}$, but optimization of magnetic performance typically requires grain alignment to achieve highest coercivity. Here we are comparing random (unaligned) magnetic powders in both the composites and pure SFO cases.

After initial precipitation, the composite powders show a decrease in magnetic properties. This is not surprising because the addition volume of antiferromagnetic $\alpha\text{-Fe}_2\text{O}_3$ dilutes SFO's remanence, saturation and energy product. The magnetic properties are improved with reduction however; Fig. 9 also shows that magnetic properties have a clear dependence on the reduction temperature.

As the reduction temperature increases, the magnetic properties improve significantly at intermediate temperatures (250–400 °C) and decrease again at 450 °C. This “optimal” temperature finding mirrors the processing window effect shown for the phase evolution (Section IIIb) and can be explained as follows. At low temperatures the soft phase has not been fully converted to the desired soft ferrimagnetic Fe_3O_4 . At reduction temperatures higher than 400 °C there is too much reaction between the SFO and the precipitated phase, forming too much of the soft ferrimagnetic phase relative to the hard ferrimagnetic phase. The maximum $(BH)_{\text{max}}$ is achieved by reducing the composite at 400 °C. Notably, all magnetic properties, except coercivity, of this nanocomposite powder surpass those of the pure SFO powder. Improvements in M_r , M_s , and $(BH)_{\text{max}}$ are 42%, 29% and 37% respectively. As noted earlier, it is likely that the $(BH)_{\text{max}}$ of these composites can be further increased by aligning the magnetic phases. This should be facilitated by the flake-like nature of our SFO and composite phases. Further studies in this direction are underway.

Fig. 10 compares the hysteresis loops of the pure SFO and the SFO/ Fe_3O_4 composite reduced at 400 °C. The smooth hysteresis curve for the composite is indicative of a single phase behavior and therefore shows evidence that the hard and soft phases are exchange coupled.³¹ If the composite was decoupled, the curve would have a clear kink resulting from the hard-soft phases acting independently.

FORC diagrams are useful for gauging particle interactions of magnetic particles. Fig. 11 shows the FORC diagram of the SFO/ Fe_3O_4 composite (Fig. 11B) as well as the pure SFO hard phase (Fig. 11A). Comparison of the two diagrams shows clear differences. The maximum value of the FORC distribution is 65×10^{-9} for the composite material and 19×10^{-9} for the SFO.

Fig. 10 SFO/ Fe_3O_4 composite (reduced at 400 °C) hysteresis loop compared to single phase SFO.

Fig. 11 First order reversal curve (FORC) diagrams for (A) single phase SFO and (B) SFO/Fe₃O₄ composite (reduced at 400 °C).

Generally, a higher maximum value indicates more ferromagnetic interactions,^{32,33} which we attribute to the existence of the soft phase in the composite.

There is also a larger spread of H_u data, suggesting more particle interactions (larger mean interaction field) in the composite material. The location of the density distribution

Fig. 12 (A) Single phase SFO recoil loop measurement. (B) SFO/Fe₃O₄ composite (reduced at 400 °C) recoil loop measurement. (C) Normalized recoil loop areas (normalized by 1/2 full hysteresis area) for pure SFO and the SFO/Fe₃O₄ composite (reduced at 400 °C). (D) Recoil remanence ratio for pure SFO and the SFO/Fe₃O₄ composite (reduced at 400 °C).

peak *i.e.* 'density hotspot' can also help interpret the nature of interactions. A hotspot located below the $H_u = 0$ axis further indicates interacting particles³⁴ and is characteristic of an exchange style interaction.³² The hotspot peak is shifted to $H_u = -236$ Oe for the composite which strongly corroborates the hysteresis curve results (Fig. 10) demonstrating exchange coupling.

To further confirm the existence of coupling in our composites, we did recoil loop measurements; recoil loop analysis has been used previously to evaluate coupling in nanocomposite permanent magnets.^{35–37} Fig. 12 shows recoil loop measurements for the SFO/Fe₃O₄ composite as well as the pure SFO hard phase, along with the recoil loop areas and recoil remanence for both the SFO/Fe₃O₄ composite and pure SFO.

In a single phase (or very well coupled) magnet, one would expect closed loops *i.e.* little to no area between the magnetization and demagnetization curves. Open recoil loops are often attributed to partial or total decoupling of the soft phases and hard phases in nanocomposite magnets.³⁸ Although not typically expected in a single composition magnet, the pure SFO exhibits open recoil loops (Fig. 12A). Open recoil loops have been reported before in nano-scale single composition magnets and attributed to inhomogeneity in magnetic anisotropy,³⁹ thermal fluctuation⁴⁰ and intergranular exchange interactions.⁴¹ We believe that one or more of these cause open loops in pure SFO. Comparison of the 'openness' of the curves in Fig. 12A and B reveals a very similar recoil behavior in the SFO/Fe₃O₄ composite and SFO.

A more quantitative comparison of the recoil loop area can be achieved by normalizing the recoil loop by 1/2 of the total hysteresis loop area. The data for the SFO/Fe₃O₄ composite in comparison to pure SFO is plotted in Fig. 12C. The fact that the open area is almost identical means that the addition of the soft phase Fe₃O₄ is not increasing the degree of decoupling of the composite compared to SFO. This is not surprising in light of the hysteresis curve and FORC analysis discussed above, showing that the SFO/Fe₃O₄ composites behave as exchanged coupled magnets.

From a permanent magnet developmental point of view, the primary reason why one wants an exchange spring behavior is to increase the energy product $(BH)_{\max}$ as we show here. Another very important benefit is to increase the magnet's resistance to demagnetization. A measure of resistance to demagnetization can be obtained by calculating the ratio of the remanence value measured during a recoil measurement, M_{recoil} (see the Experimental procedure for details) to the M_r measured during a standard hysteresis loop. This ratio is plotted for the nanocomposite and SFO in Fig. 12D. An exchange coupled nanocomposite magnet with an optimal microstructure has a partially reversible demagnetization curve,⁴² meaning that at low H_a values, the M_{recoil}/M_r ratio is close to 1. We see that this is the case for the recoil remanence ratio (Fig. 12D) of the nanocomposites. The data also reveal that the M_{recoil}/M_r values are higher for the SFO/Fe₃O₄ composite than the pure SFO at all applied magnetic fields, demonstrating that the composites are more resistant to demagnetization and providing further evidence of exchange coupling.

Summary

In summary, we have presented a synthesis and processing procedure for the production of SFO/Fe₃O₄ exchange coupled nanocomposites that contain no rare earth or precious metals. Our procedure is a simple scalable procedure that relies on a precipitation step followed by a reaction step. The precipitation step ensures intimate contact and good intermixing of the two phases. The reaction step allows for the conversion of the as-precipitated precursor to convert to the desired magnetic soft phase (Fe₃O₄). The data presented clearly show that there is a limited processing temperature window that produces the desired phase. Magnetic measurements reveal that the $(BH)_{\max}$ of the SFO/Fe₃O₄ composite powders is 37% higher than the pure SFO hard phase, confirming that the evasive goal of a rare earth free PM material can be realized using the procedure presented here. These core/shell powders could potentially be densified and used in PM motor/generator applications and/or biomedical applications.

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