Exchange-spring behavior in $\text{BaFe}_{12}\text{O}_{19}\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposites synthesized by a combustion method

Rui Xiong*, Weiwei Li, Chunlong Fei, Yong Liu, Jing Shi

Abstract

Exchange-spring systems offer various technological applications. In this study, $\text{BaFe}_{12}\text{O}_{19}\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite magnets with single-step hysteresis loops were synthesized through a simple combustion method. Their composition, microstructure, and magnetic properties were also investigated. It was found that the magnetic properties and the mechanisms governing the magnetization of these nanocomposite magnets are strongly influenced by the calcination temperature as well as the molar ratios of the hard and soft phases. The exchange-coupling between the hard and soft magnetic phases was confirmed by the study of Henkel plots and the variation in the magnetic properties could also be explained by the dominant role of exchange and dipolar interactions in the nanocomposites. The study provides a simple but efficient route for the fabrication of exchange-coupled nanocomposite magnets based on ferrites having controllable magnetic properties.

Keywords: $\text{BaFe}_{12}\text{O}_{19}\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nano-composite; exchange spring behavior; magnetic properties; Henkel plots

Introduction

In recent years, exchange-spring systems have gained considerable attention owing to their application in the improvement of magnetic properties.^[1-5] The concept of exchange-spring behavior was put forward in the early 1990s by Kneller et al.^[6] Later, Skomski and Coey^[7] proposed that the predicted magnetic energy product of ordered nanocomposites can reach up to 1 MJ/m³ in theory, which is much larger than that of sintered Nd-Fe-B magnets (445 kJ/m³).^[8] In the last few decades, a lot of effort has been made through theoretical as well as experimental studies to obtain materials with a high magnetic energy product. These studies mainly focused on two kinds of materials: 1) alloy composites-based permanent magnets like Nd-Fe-B, FePt, and Sm-Co^[9-12] because of their high magnetic energy products and 2) oxide composite materials such as CoFe₂O₄/Fe₃O₄, CoFe₂O₄/CoFe₂, BaCa₂Fe₁₆O₂₇/Fe₃O₄, and BaFe₁₂O₉/Ni_{0.8}Zn_{0.2}Fe₂O₄^[13-16] owing to their inexpensive synthesis and high corrosion resistance. However, it is difficult to realize the exchange-spring principle in hard-soft ferrite nanocomposites because of the intricate fabrication methods and microstructural complexities involved.^[17] In order to achieve homogeneously distributed hard-soft ferrite nanocomposites, a simple but efficient fabrication method is imperative.

The combustion method has gained popularity as a simple but efficient method for the fabrication of a variety of materials such as Ba-hexaferrite, NiZn ferrite, and CoFe₂O₄.^[18-21] Recently, some studies focusing on the fabrication of a hexaferrite/NiZn ferrite composite material using this method have been reported.^[22-23] In their work, both hard and soft magnetic phases were simultaneously synthesized by the combustion method. Compared to the other methods, this “one-pot” method offers many advantages including simplicity and homogeneity. Moreover, this method can be used to fabricate exchange-spring magnets in which the average diameter of the soft phase is less than twice the domain wall width of the hard phase, which should be the case to achieve an exchange-coupling beneficial to the magnetic properties of such magnets.^[7] However, these magnets usually show two-step hysteresis loops indicating that the hard and soft phases have not undergone sufficient exchange coupling at the interfaces.

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5 In the present work, hard-soft $\text{BaFe}_{12}\text{O}_{19}\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite magnets were
6 simultaneously fabricated by the combustion method. By controlling the fabrication conditions,
7 homogeneously distributed hard-soft nanocomposite magnets that exhibit single-step magnetic
8 hysteresis loops were fabricated. The nature of magnetic interactions in these composites and
9 their magnetic properties were investigated in detail using the Henkel plot.
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15 Experiment details

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17 The hard-soft $\text{BaFe}_{12}\text{O}_{19}\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite magnets were simultaneously
18 fabricated by using the combustion method. An appropriate amount of metal nitrates and citric
19 acid was dissolved in de-ionized water followed by the addition of ammonia solution to adjust
20 the pH to 7. The resulting solution was then heated to 300 °C until the formation of a gel and its
21 subsequent combustion. Finally, the resulting powders were calcined in air at 750, 800, 850, 900,
22 or 1000 °C for 2 h in order to obtain a ferrite structure. The samples were then labeled
23 accordingly; for example, H/S-70/30-800 denoted the sample with a hard: soft molar ratio of
24 70:30 calcined at 800 °C for 2 h.
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34 XRD patterns were collected using a D8-Advanced X-ray diffractometer (XRD) with Cu α
35 radiation ($\lambda = 1.5418$ Å). The morphologies of the nanocomposites were observed by a scanning
36 electron microscope (SEM, FEI SIRION) as well as a high resolution transmission electron
37 microscope (HRTEM, JEM 2010 FEF). The magnetic hysteresis loops and the Henkel plots
38 were measured at 300 K using a vibrating sample magnetometer (VSM) on a physical property
39 measurement system (PPMS-9, Quantum Design).
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47 Results and discussion

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49 FIG. 1(a) shows the XRD patterns of the H/S-70/30 nanocomposites calcined at different
50 temperatures. The XRD patterns of the samples calcined at 750 °C and 800 °C show the presence
51 of BaFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ impurity phases. At higher calcination temperatures, only $\text{BaFe}_{12}\text{O}_{19}$
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58 The XRD patterns of the $\text{BaFe}_{12}\text{O}_{19}\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposites with different molar
59 ratios calcined at 1000 °C are shown in FIG. 1(b). As can be seen, the characteristic peaks for
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both the hard ($\text{BaFe}_{12}\text{O}_{19}$) and soft ($\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) phases are observed and no extra peak is detected within the resolution of the diffractometer.

FIG. 2 shows the SEM, TEM, and HRTEM images of the H/S-70-30-1000 nanocomposite. The average diameter of the particles was estimated to be about 100 nm. The HRTEM images confirm the presence of the hard and soft magnetic phases and indicate their boundaries. The insets in FIG. 2 provide details of the inter-planar distance in both the phases. The lattice fringes matched well with the theoretical reflections for $\text{BaFe}_{12}\text{O}_{19}$ (P6/mmm symmetry) and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (Fd 3m atomic model).

FIG. 3(a) shows the magnetic hysteresis loops of the H/S-70/30 nanocomposites calcined at different temperatures. It can be observed that there exists a two-step hysteresis loop for the powder calcined at 750 °C. The powder calcined at 800 °C shows a much smoother hysteresis loop. The powders calcined at temperatures higher than 800 °C show single-step hysteresis loops, indicating the occurrence of strong exchange-coupling at the interfaces between the hard and soft magnetic phases. If the exchange-coupling is not strong enough, the resulting hysteresis loop would be the superimposition of two loops corresponding to the soft and hard phases.^[14]

Saturation magnetization (M_s) was obtained by fitting the initial magnetization curve (above 45,000 Oe) using the Law of Approach to Saturation.^[24]

$$M = M_s - \frac{0.07619K_{eff}^2}{MsH^2} + \chi_p H \quad (1)$$

where M and H denote the magnetization and applied magnetic field, respectively, and A is a parameter which is related to the effective magnetic anisotropy constant. The final term represents the magnetization contributed by the paramagnetic magnetization process at a high field. Remanence (M_r) and coercivity (H_c) were determined by linear fitting the data near $H=0$ Oe and $M=0$ emu/g, respectively.

The magnetic properties of the nanocomposites calcined at different temperatures are shown in FIG. 3(b). As can be seen, M_s as well as M_r increased with an increase in the calcination temperature. H_c shows a maximum value at 800 °C, which starts decreasing as the calcination

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5 temperature is increased further. It is well-known that an increase in calcination temperature
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7 leads to an increase in average particle size. This might have contributed to the increase in M_s
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9 and M_r . According to micromagnetic calculations, the size of soft grains should ideally not be
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11 larger than twice the domain wall width of the hard magnetic phase.^[7] The increase in grain size
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13 increases the dipolar interactions among the soft phases and enervates the exchange force
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15 between the hard and the soft phases. As a result, the reverse domains in the soft phases with low
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17 nucleation field can be nucleated easily, thus decreasing the coercivity.

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19 The magnetic hysteresis loops for the samples calcined at 1000 °C with different molar
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21 ratios are shown in FIG. 4. It is observed that all the samples show single-step hysteresis loops.
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23 The magnetic properties are listed in Table 1. The magnetic property of the two-phase
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25 nanocomposite magnet is closely related to the ratio of the soft magnetic phase. The M_r/M_s ratio
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27 was found to be close to 0.5, which is the optimum value for coherent magnetization rotation.^[25]
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29 The coercivity decreases monotonically with the volume of the soft phase. As the volume of the
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31 soft phase increases, the role of dipolar interactions among the soft grains becomes more
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33 important^[26] and the reverse domains in the soft phase with low nucleation field nucleate readily.
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35 Thus, the value of H_c decreases.

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38 The Henkel plot provides some insight into the interaction mechanisms governing the
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40 magnetization processes.^[27] The δm curves were built using the magnetizing ($M_r(H)$) and
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42 demagnetizing ($M_d(H)$) remanent magnetizations that were measured as follows. Upon attaining
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44 the desired experimental temperature, a small external field H was applied to the sample for a
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46 certain period of time. The remanent $M_r(H)$ was then measured. The process was repeated with
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48 gradually increasing magnitudes of H until the sample reached a saturation state and $M_r(H)$
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50 attained the saturation value $M_r(\infty)$. Next, the remanent demagnetizing magnetization was
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52 obtained by following an approach similar to that followed to obtain $M_r(H)$. Starting with the
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54 saturation state, a small external field H was applied to the saturated sample in a direction
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56 opposite to magnetization. After some time, the field was removed and $M_d(H)$ was measured.
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58 This was repeated again with the magnitude of H being gradually increased until saturation was
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attained in the opposite direction. Finally, $Mr(H)$ and $Md(H)$ were normalized by $Mr(\infty)$: $Mr=Mr(H)/Mr(\infty)$ and $md=Md(H)/Md(\infty)$. The variation of δm with the applied field was investigated where $\delta m=md(H)-[1-2Mr(H)]$.

FIG. 5 shows a graph of m_d as a function of H for the nanocomposites calcined at 850 and 1000 °C. The graph clearly indicates that the mechanisms governing the magnetization process are strongly influenced by the calcination temperature.

The nature of interactions in a set of magnetic nanoparticles has been determined by using the Wohlfarth relationship established for non-interacting uniaxial nanoparticles, $md=1-2Mr$ ^[28]. A deviation from the Wohlfarth relationship indicates that the nanoparticles interact among themselves as shown in FIG. 6. This deviation is better seen through a relationship known as δm .

A positive value of δm corresponds to exchange-interactions between the soft and hard phases of the nanocomposites. A negative value of δm corresponds to dipolar interactions in the nanocomposites.^[26] As can be seen from FIG. 7, the magnitude of δm for H/S-70/30-850 is negative under all fields, while for H/S-70/30-1000, positive values are also observed. A similar behavior has been observed in some metallic alloys.^[29] As is known, with an increase in calcination temperature, the sizes of both the hard and soft magnetic phases increase. The refinement of the crystalline regions of the hard magnetic phase can be attributed to the existence of inter-particle exchange-coupling. The observed increase in the size of the negative peak may be attributed to the increase in dipolar interactions, which is in agreement with the magnetic measurements.

FIG. 8 shows the δm of the samples with different molar ratios calcined at 1000 °C. For H/S-50/50-1000, the magnitude of δm is negative under all fields, indicating the presence of dominant inter-particle dipole interactions. For H/S-70/30-1000 and H/S-90/10-1000, positive peaks are also observed. The intensity of these positive peaks increases with a decrease in the volume of the soft phase, which indicates that there is an increase in the inter-particle exchange-coupling. This result is consistent with the variation in magnetic properties.

Conclusions

We successfully fabricated exchange-coupled $\text{BaFe}_{12}\text{O}_{19}\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocomposite magnets with single-step hysteresis loops using a simple combustion method. The magnetic measurements revealed the exchange-spring behavior of these nanocomposites. The inter-particle interactions were studied using δm plots. The nanocomposites were found to exhibit inter-particle exchange coupling. The magnetic properties and the mechanisms governing the magnetization process were found to be strongly influenced by the calcination temperature as well as the weight ratios of the hard-soft phases. Though the optimum processing conditions still need further investigation in order to achieve high values of $(BH)_{\max}$, this study promotes the possibility of synthesizing exchange-coupled nanocomposites based on ferrites having controllable magnetic properties for practical use through a simple chemical reaction.

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Figure Captions:

FIG. 1a. XRD pattern of sample H/S-70/30 calcinated at different temperatures from 750 to 1000°C

FIG. 1b. XRD pattern of $\text{BaFe}_{12}\text{O}_{19}\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nano-composites with different molar ratios calcinated at 1000°C

FIG. 2. SEM, TEM, HRTEM images of the sample H/S-70/30-1000

FIG. 3a. Magnetic hysteresis loops of the samples H/S-70/30 heated at different temperatures.

FIG. 3b. The magnetic properties (M_s , M_r , H_c) of samples H/S-70/30 calcinated at different temperatures.

FIG. 4. The magnetic hysteresis loops of nano-composites with different weight ratios calcinated at 1000°C

FIG. 5. Graph of md as a function of H for sample H/S-70/30 calcined at 850 and 1000°C

FIG. 6. Henkel plots for sample H/S-70/30 calcined at 850 and 1000°C

FIG. 7. δm plots of sample H/S-70/30 calcined at 850 and 1000°C

FIG. 8. δm plots of samples with different molar ratios calcinated at 1000°C

TABLE I. Magnetic properties of nano-composites with different molar ratios calcinated at 1000°C

Figure 1a

Figure 1b

Figure 2

Figure 3a

Figure 3b

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1

Sample	M_r/M_s	$H_c(\text{Oe})$
H/S-100/0	0.48	4766.7
H/S-90/10	0.5	4112.6
H/S-70/30	0.49	3526.8
H/S-50/50	0.47	2906.1
H/S-0/100	0.002	7.7