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Exchange spring magnetic behavior in $BaFe_{12}O_{19}/Fe_3O_4$ nanocomposites

K.P. Remya [a], D. Prabhu [b], S. Amirthapandian [c], C. Viswanathan [a], N. Ponpandian [a,*]

[a] Department of Nanoscience and Technology, Bharathiar University, Coimbatore 641 046, India
[b] Centre for Automotive Energy Materials, ARCI, Chennai 600 113, India
[c] Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

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ABSTRACT

We report the investigation on exchange spring coupling behavior of $BaFe_{12}O_{19}/Fe_3O_4$ nanocomposite synthesized by simple mixing followed by heat treatment of individual ferrites. Morphologically tuned, well crystalline hard and soft ferrites were synthesized by simple chemical method and the phase composition, crystallinity, surface morphology and magnetic properties of the as prepared ferrites as well as the nanocomposites were studied by using XRD, FESEM and VSM respectively. Exchange coupling behavior is observed in the nanocomposite samples heated at 600 °C with simultaneous enhancements of $(BH)_{max}$ and remanence.

1. Introduction

The interest in research and development in the field of nanostructured magnetic materials has been increasing both from the fundamental physics and the technological points of view as these materials exhibit many unique and interesting physical and chemical properties. Nanocomposite materials that constitute fine mixture of hard and soft magnetic phases show enhanced properties which make them suitable for various potential applications including permanent magnets [1–4]. In addition to the size, shape and distribution of the constituent grains, the exchange as well as the dipolar interaction also plays an important role in the magnetic property of a two phase magnetic nanocomposite. In order to realize the improved properties of these materials, the hard and soft magnetic phases are exchange-coupled so that the hard phase magnetization with higher coercivity (H_c) combines with the high magnetization (M_s) of the soft phase. The characteristic exchange spring behavior occurs when the applied magnetic fields are not large enough to reverse the hard magnetic phase while the soft magnetic phase undergoes reversible rotation [5]. Many research groups have investigated the fundamental mechanism of exchange interaction, magnetization and demagnetization behavior in nanostructured single-phase as well as composite materials to understand their exchange-spring coupling characteristics [6,1], employing different techniques, such as melt-spinning [7,8], mechanical alloying [9,10], sputtering [11,12], self-assembly [13], *etc.*, for their preparation. Recently intensive investigations are being done on ferrite composite powders owing to their simple methods of preparation and ease of tuning the magnetic properties with microstructural distribution of the hard and soft magnetic phases, including $CoFe_2O_4/ZnFe_2O_4$ [14], $SrFe_{12}O_{19}/ZnFe_2O_4$ [15], $SrFe_{12}O_{19}/ Ni_{0.7}Zn_{0.3}Fe_2O_4$ [16], $BaCa_2Fe_{16}O_{27}/Fe_3O_4$ [17], $BaFe_{12}O_{19}/Ni_{0.8}Zn_{0.2}Fe_2O_4$ [18]. $BaFe_{12}O_{19}/ CoFe_2O_4$ [19] and the reports showed excellent exchange coupling and enhanced remanence in some of these systems while others presented enhanced coercivity with decrease in magnetic saturation.

Among different systems, those combining hexagonal ferrite with spinel/ inverse spinel ferrite have obtained noticeable attention by researchers. $BaFe_{12}O_{19}$, a well-known hard magnet is a hexagonal ferrite having high coercivity, high curie temperature, good mechanical hardness, superior chemical stability and corrosion resistance [20–22], making it suitable for different applications such as permanent magnets, magnetic recording media, magneto-optical materials and microwave filters, *etc.*, [23–26]. However, these technological applications require well defined micro structure, controlled homogeneity, particle size and magnetic characteristics. A wide range of synthetic methods starting from chemical co-precipitation to aerosol pyrolysis have been employed for the successful synthesis of these M-type barium ferrites focusing on the nanoscale size distribution of the material in order to improve their magnetic properties [27–30].

Superparamagnetic Fe_3O_4 nanoparticles have enticed much

* Corresponding author.

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interest not only in magnetic recording media, magnetic fluids, and data storage but also in the fields of catalysis, hyperthermia and targeted drug delivery [31–36]. Other than conventional methods, chemical synthesis such as co-precipitation, sol–gel method, ultrasound irradiation, hydrothermal method, polyol method, *etc*. have been described to produce Fe_3O_4 nanoparticles [37–39]. Among transition metal oxides, magnetite exhibits the strongest magnetism in which the strong magnetic moment of iron atom comes from the four unpaired electrons in its 3d orbitals. Magnetite is ferrimagnetic at room temperature having a Curie temperature of 850 K [40,41]. Synthetic methods and crystal morphology seems to have strong influence on the magnetic properties of these nanoparticles and coercivities ranging from 2.4 to 20 kA/m and magnetic saturation (Ms) of ~75 emu/g have been obtained by controlling their synthesis conditions [40].

In the present work we have prepared $BaFe_{12}O_{19}/Fe_3O_4$ nanocomposite ceramics by a novel and simple method to understand exchange spring behavior in ferrite composites. Respective oxides with suitable microstructure were prepared using plain chemical methods, succeeded by mixing and proper heat treatment of the individual single phases. The simultaneous enhancements in remanence and in $(BH)_{max}$ compared with the parent hard ferrite ($BaFe_{12}O_{19}$) has been achieved.

2. Experimental

2.1. Synthesis of $BaFe_{12}O_{19}/Fe_3O_4$nanocomposite

The precursors used for the present investigation includes, barium nitrate, ferric nitrate and ferric chloride, i.e., $Ba(NO_3)_2$, $Fe(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$ (purity > 99%, sdFine), sodium hydroxide (NaOH) and urea were used as base medium and ethylene glycol and deionized water were the solvent medium. All the chemicals are analytically graded and used without further purification. The ferrites were synthesized separately by simple hydrothermal/solvothermal methods. The synthesis of the hard ferrite, barium ferrite nanoparticles ($BaFe_{12}O_{19}$) has been carried out by dissolving 1:12 ratio of $Ba(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ respectively, in distilled water followed by the addition of NaOH drop wise for the precipitation to occur. After stirring for 30 min, the resulting suspension was transferred to an autoclave having capacity of 70 ml and heated to 200 °C for 12 h. The obtained hydrothermal product was washed several times with water and ethanol and dried overnight at 70 °C. The synthesis of the soft ferrite, magnetite nanoparticles (Fe_3O_4) was done by solvothermal method. In a typical process 0.5 mol $FeCl_3 \cdot 6H_2O$ was dissolved in ethylene glycol followed by the addition of required amount of NaOH and urea. The resultant suspension was vigorously stirred for 30 min and transferred to an autoclave which was heated at 200 °C for 12 h. The black product was washed many times with water and ethanol and dried overnight at 70 °C.

The preparation of $BaFe_{12}O_{19}/Fe_3O_4$ nanocomposite has been done by mixing the soft and hard ferrite in different weight ratios such as 3:1, 6:1 and 9:1 respectively. The samples were divided into three batches which were heat treated at three different temperatures to realize the effect of temperature on the magnetic property of the composite. The samples were heat treated at 100, 300 and 600 °C for a time period of 2 h.

2.2. Characterizations

The samples were characterized by means of X-ray diffraction using X-ray difractometer with high intensity Cu Kα radiation (Rigaku D/MAX -2400). The surface morphology of the samples was determined by using field-emission scanning electron microscope (FESEM, FEI quanta-250) equipped with energy dispersive X-ray spectroscopy (EDS). Magnetic hysteresis loops were measured by using vibrating sample magnetometer (VSM, EG&G Parc, Model 4500) at room temperature.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of pristine $BaFe_{12}O_{19}$ (BaM), Fe_3O_4 nanoparticles and the nanocomposite of $BaFe_{12}O_{19}/Fe_3O_4$ with different ratios such as 9:1, 6:1 and 3:1 heat treated at 600 °C for 2 h are shown in Fig. 1. Fig. 1(a) shows the crystalline structure of pure Fe_3O_4 nanoparticles. The observed patterns are indexed with the standard JCPDS # 89-2355. The diffraction peaks of (220), (311), (400), (422), (511) and (440) reflect the magnetite crystal with cubic spinel structure [42]. The average grain size of the prepared magnetite nanoparticles estimated from the full width at half maximum (FWHM) using Scherrer formula is found to be 59 nm.

The XRD pattern in Fig. 1b indicates a pure hexaferrite phase with all the major diffraction peaks matching the crystalline $BaFe_{12}O_{19}$ corresponds to JCPDS # 27-1029. All peaks belong to the phase of *M* type barium ferrite (magnetoplumbite) and no other impurity was observed. The average grain size estimated for the nanostructured hard ferrite is found to be 78 nm. Fig. 1(c, d and e) shows the diffraction patterns for the nanocomposite with the BaM/Fe_3O_4 ratios of 9:1, 6:1, 3:1 respectively. All these diffraction patterns clearly show the characteristic diffraction peaks for BaM (*) and Fe_3O_4 (**o**) and no other impurity peak or change in peak position has been observed even after the samples are heat treated. The XRD patterns of nanocomposite also shows the peaks correspond to the soft ferrite phase are broader when compared to those of barium ferrite confirming the small size of soft magnetic phase in the nanocomposite. So it can be confirmed that the composite consists of two independent phases irrespective of chemical treatment.

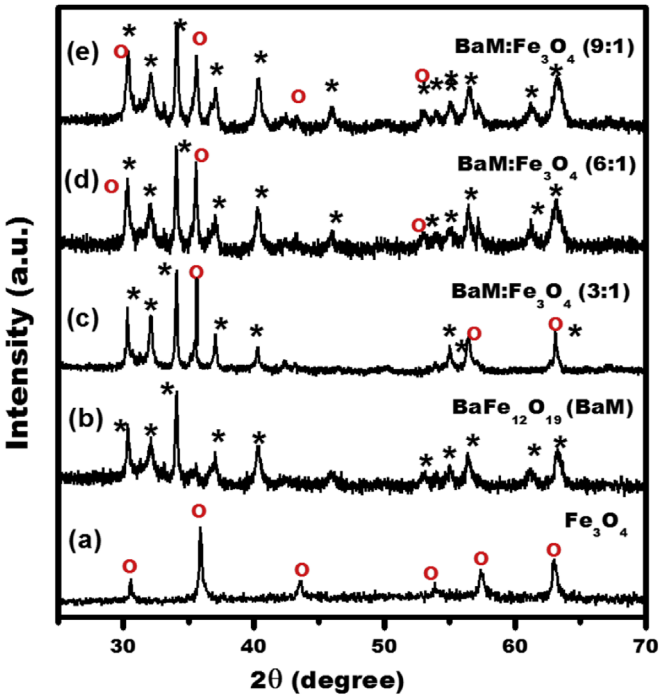

Fig. 1. X-ray diffraction pattern of (a) Fe_3O_4 nanoparticles, (b) $BaFe_{12}O_{19}$, $BaFe_{12}O_{19}/Fe_3O_4$ nanocomposite mixed in ratio (c) 3:1, (d) 6:1 and (e) 9:1 respectively and heat treated at 600 °C for 2 h.