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Formation and characterization of magnetic barium ferrite hollow fibers with low coercivity via co-electrospun

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ABSTRACT

$BaFe_{12}O_{19}$ fibers and hollow fibers were successfully prepared by electrospun and co-electrospun. A very interesting result appeared in this study that hollow fibers made by co-electrospun showed low coercivity values of a few hundred oersteds, compared with the coercivity values of more than thousand oersteds for the fibers made by electrospun. So the hollow fibers with high saturation magnetization (M_s) and while comparatively low coercivity (H_c) exhibited strong magnetism and basically showed soft character. And this character for hollow fibers will lead to increase of the permeability for the samples which is favorable for impedance matching in microwave absorption. So these hollow fibers are promised to have use in a number of applications, such as switching and sensing applications, electromagnetic materials, microwave absorber.

1. Introduction

According to the material loss mechanism, the electromagnetic wave absorber can be divided into resistive, dielectric and magnetic medium type. Barium ferrite ($BaFe_{12}O_{19}$) belongs to magnetic medium type absorber. And this type absorbs microwave by resonance and magnetic hysteresis loss.

As we all know, the barium ferrite has frequently been used as hard magnetic magnets due to its large saturation magnetization and large uniaxial magnetic anisotropy in a longitudinal direction (*c*-axis) [1]. And a wide span of other applications in electromechanical and electronic devices, magnetic recording media and microwave absorption materials owing to its high chemical and thermal stability, adjustable anisotropy and corrosion resistance. But good impedance matching is very important for absorbing materials. So in order to improve the absorbing properties, we aim to increase the saturation magnetization, and at the same time reduce the coercive force.

But it is hard to make the saturation magnetization to achieve the theoretically estimated values due to the surface spin-canting phenomenon, purity and particle size effects, morphology and so on [2–4]. So In order to improve the magnetic property and broaden their applications, we purpose to reduce the coercivity.

As we all know, the coercivity is mainly influenced by the morphology. So the key challenge is to obtain required properties by control morphology and properties. A lot of research have been made on element doping (Sr [5,6], Pr [7], Al [8], etc.) and special morphology preparation, for instance $BaFe_{12}O_{19}$ fibers [6], tubes [2,9], belts, etc. However, the coercivity data for these ferrites was several thousand which will also limit their application in which need high magnetization and low coercive force such as switching and sensing applications, electromagnetic materials, microwave absorbing materials and so on.

So far there are several kinds of morphology for barium ferrite, a hexagonal flake, globularity, rod-like morphology, acicular morphology, fibers. Currently the researches mainly concentrate on the zero dimensional particles and one-dimensional fibers. Refs. [1,10] have prepared barium ferrite particles with coercivity 910 Oe and 1200 Oe respectively which are lower than that of ordinary $BaFe_{12}O_{19}$. Comparatively the coercivity of barium ferrite fibers is still several thousand. But the 1D nanofibers have great potential applications in filtration materials [1112], membrane separations materials [13], catalysts [14], biomedical materials [15] and many other industries because of their unique structures [2], low density, high aspect ratio, specific surface. Especially hollow fibers, this type of morphology is of interest for the aqueous environment, the storage and controlled release of drugs [16] due to higher specific surface area. It has been reported that hollow fibers could produce a significant increase in performance in filtration compared to non-hollow fibers made by the single-jet process [9,17,18]. So we can deduce it is possible to prepare 1D barium fibers with coercivity on the order of several hundred or even less.

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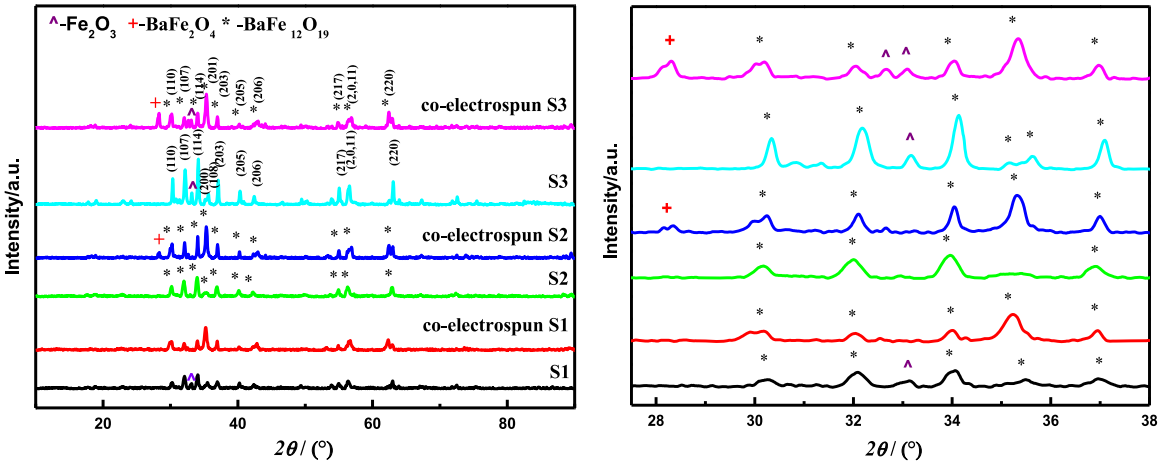

Fig. 1. XRD patterns for all $BaFe_{12}O_{19}$ samples ranged 10 – 90° (a) and 27 – 38° (b).

Several methods could be used to prepare hollow fibers, such as electrospinning [19], template [20], sol–gel methods [21] and gel-thermal selective reduction process [22]. As compared to other methods, coaxial electrospun has been proved to be a simple and versatile process for manufacturing continuous hollow fibers of multiplicity materials, such as metal, metal oxides and ceramic [16,23] with diameters ranging from a few nanometers to microns. Furthermore, this method provides access to prepare entirely new materials with complex chemical structures. Electrospun appears to be a straightforward method, but is rather intricate that depends on a multitude of molecular, the nature of the precursor solution, external environment condition (temperature, humidity etc.) during the process and technical parameters. So in this study we aim at researching hollow $BaFe_{12}O_{19}$ fibers via co-electrospun by control the factors and research the effect of the fibrous hollow structure to the magnetic performance. As a result, the coercivity drop to several hundred from several thousand, consequently expand the range of application in sensor materials, electromagnetic materials etc. and increase the permeability of the sample which is favorable for impedance matching in microwave absorption [7,24].

2. Experimental

All the raw materials barium nitrate [$Ba(NO_3)_2$, AR], ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$, AR], dimethyl formamide (DMF) and Poly Vinyl Pyrrolidone (PVP) used to synthesize $BaFe_{12}O_{19}$ fibers were analytical grade and purchased from Sinopharm Chemical Reagent co., ltd, Shanghai, China.

In this experiment progress, we prepared three groups samples named S1, S2 and S3 respectively. Appropriate amount (a molar ratio of Fe/Ba is 12:1, 11.5:1 and 11.5:1 separately) of $Ba(NO_3)_2$, and $Fe(NO_3)_3 \cdot 9H_2O$, were dissolved in 20.0 ml DMF. And then after adding appropriate amount of PVP (M_w = 1,300,000) into the above three groups solution, the precursor solution was stirred until became homogeneous transparent brown solution. After laid for about two hours to eliminate air bubbles in the solution, the stable sol was obtained.

In a typical electrospinning process, the precursor sol was transferred into a syringe connected to a metallic nozzle, and fed at a constant rate of 0.05 mm/min through a syringe pump. In a coaxial process, a special nozzle which was made by combining two concentrically aligned nozzles with different inner diameter must be used for spinning to produce core–shell fibers, and then remove the core, finally hollow fibers were successfully prepared. So in this process, two viscous but immiscible liquids, sesame oil and a dimethyl formamide solution containing PVP and barium and iron nitrate were used as the source materials for core and sheath. A distance of 15 cm and voltage of 15 kV were maintained between the tip of the spinneret and the collector. In order to fabricate uniform fibers we use a rotary drum as the collector. The metallic nozzle was connected to a high voltage supply, and the collector was connected to a low voltage supply. Upon applying a high voltage of 13 kV, a deform compound droplet was created, and then a fluid jet was ejected from the metallic nozzle. While in the coaxial electrospun, the same voltage is applied to both nozzles, the inner droplet would could be directly incorporated into the interiors of fibers as they were electrospun from the spinneret [16,19]. In an ideal case, the solvent evaporated, finally the charged gel fibers and core–shell fibers were deposited on the collector. In order to prepare enough fiber for testing, the collecting time of fiber arrays was about 5 h. All experiments were conducted at room temperature in air [2,25,26].

After electrospinning, these precursor fibers were first dried in the drying oven in air atmosphere at 80 °C and then calcined at 800 °C for 2 h in a box furnace in air to obtain the fibers with different morphology.

The X-ray diffraction (XRD) patterns were collected on a diffractometer with Cu-Kα radiation (the wavelength λ = 0.154 nm). The images of the samples were investigated by scanning electron microscopy (SEM) and transmission electron microscope (TEM). The magnetic hysteresis loops of the magnets were measured at room temperature using a vibrating sample magnetometer (VSM, HH-15) in applied maximum magnetic field up to 1.2 T [27,28]. Agilent 8722ET vector network analyzer (VNA) was applied to determine the complex permittivity and permeability in the frequency range of 2–18 GHz for the calculation of reflection loss. The samples containing 16.7 wt% obtained products were pressed into a ring with an outer diameter of 7 mm, an inner diameter of 3 mm, and a thickness of 1–2 mm for microwave measurement in which paraffin wax was used as the binder.

3. Results and discussion

3.1. Structural analysis

The XRD patterns of $BaFe_{12}O_{19}$ samples for phase identification performed by the X-ray diffraction (XRD) are shown in Fig. 1. The presence of the diffraction peaks in the patterns of S1, S2 and S3 corresponding to the planes (1 1 0), (1 0 7), (1 1 4), (2 0 0),(1 0 8), (2 0 3), (2 0 5), (2 0 6), (2 1 7), (2 0 11) and (2 2 0) indicates that the studied samples have M-type hexagonal structure according to standard JCPDS card no. 39-1433 with space group P63/mmc. The