Journal of Alloys and Compounds 618 (2015) 222–226

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Preparation and microwave absorption properties of Ni–Co nanoferrites

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ARTICLE INFO

Article history:
Received 9 June 2014
Received in revised form 19 August 2014
Accepted 23 August 2014
Available online 1 September 2014

Keywords:
Ni–Co nanoferrites
Magnetism
Absorbing property
Microwave
Ball milling

ABSTRACT

$Ni_xCo_{1-x}Fe_2O_4$ ($x = 0.2$, 0.5, 0.8) particles were prepared by a self-designed method, i.e., microwave assisted ball milling. A series of characterizations were carried out on the prepared powders, including X-ray Diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM) and vector network analyzer (VNA). XRD and TEM results indicated that the particles are well-crystallized and the average size is about 15 nm. According to VSM results, the M_s values are 76 emu/gm, 61 emu/gm and 46 emu/gm respectively, which obviously presented higher saturation magnetization values compared with other existing methods. Complex permittivity and permeability of Ni–Co ferrites were explored by VNA in the frequency of 2–18 GHz, and the reflection loss (RL) was also calculated. The results illustrated that the minimum reflection loss values of the three ferrites all emerged in the range of 9–12 GHz, and the $Ni_{0.8}Co_{0.2}Fe_2O_4$ with a thickness of 2.5 mm could achieve −36.2 dB at 11.52 GHz, which indicated that the Ni–Co ferrite nanoparticles possessed great potential in microwave absorption applications.

1. Introduction

In recent years, nanoferrites, as a new type of nano-substance, have attracted much attention on account of their extensive use in pharmaceutical, chemical, aerospace, military and other important fields [1–3]. Due to their distinctive properties exhibited in biological, electrical, magnetic and surface reactivity, they have become an indispensable substance in many products [4–6]. High coercivity, moderate saturation magnetization, large anisotropy, and mechanical hardness, all make ferrites a good candidates in magnetic sensors, data storage, electromagnetic wave absorbers, magnetic composites and information delivery devices [7–10]. Furthermore, various kinds of ferrites exhibit outstanding microwave absorption properties and have been widely employed in military and civil fields as microwave absorbers because of their high absorption rate, broad absorption band and thin matching thickness [11–13].

Obviously, interesting and useful properties of spinel ferrites have driven more and more scientists to look into their preparation, reporting a number of investigations. Maaz and Kim [14] prepared Ni–Co ferrite by a chemical coprecipitation route, which explained the relations of M_s. (saturation magnetization), H_c (coercivity), d_{sdl} (single domain size) and content. Yue et al. [15] reported the sol–gel preparing process and properties of NiCuZn ferrite and proved its superior frequency stability and higher-quality factor compared to other conventional ceramic routes. Shenoy et al. [20] investigated the high-energy ball milling to compound $ZnFe_2O_4$ and found the anomalous behavior and Dielectric behavior. Meanwhile, preparation methods like self-propagation [16,17], hydrothermal [18,19] and mechanical milling [21] all have been widely used in synthesizing ferrites. However, ferrites prepared by traditional methods ways exhibit two weaknesses that limited their further development: (1) over-sized grain (2) high anisotropy.

Recently, a new synthesis method developed by our group, i.e., microwave assisted ball milling solved these two limitations [22–24] On one hand, the grains could be broken by ball milling, eventually obtaining nano-sized powders. On the other hand, the substitution of divalent-tetravalent (Co^{2+}, Ni^{+}) to Fe^{3+} would effectively reduce the high anisotropy [25–27]. Furthermore, this mechanochemical approach not only combines the advantages of microwave and milling methods, but also only requires simple operation and inexpensive equipment. In this present paper, the successful synthesis of $Ni_xCo_{1-x}Fe_2O_4$ ($x = 0.2$, 0.5, 0.8) nanoferrites by microwave assisted ball milling was reported and their magnetic and microwave absorption were studied.

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http://dx.doi.org/10.1016/j.jallcom.2014.08.195
0925-8388/

2. Experimental

The microwave assisted ball-milling device designed by the authors' group is shown in Fig. 1. In the experiment, the mixed solution was put into a milling tank to accept the coupling function of microwave and milling.

Nickel–cobalt-oxide and iron powder were used as the raw materials to prepare $Ni_xCo_{1-x}Fe_2O_4$ with different Ni/Co ratios (x = 0.2, 0.5, 0.8) by the method of microwave assisted ball milling. The brief process is as follows: stainless steel balls (1.5 mm in diameter) and raw materials were mixed with the ratio of 100:1; the power and frequency of the microwave were 1.2 kW and 2450 MHz respectively; the stirring speed was 256 r/min. During the experiment, the mixture was milled without microwave assistance in the first 15 min, then the microwave was turn on for 15 min. This operation alternated repeatedly for 60 h. The mixed aqueous solution was then taken out to wash and dry. The obtained powder was then detected by the following equipments:

Structural and morphology characterization were performed by X-ray diffraction (D-5000, Siemens, Cu Kα) and transmission electron microscopy (TEM, JEOL-1230). The magnetic properties of three kinds of powders were characterized by vibrating sample magnetometer (VSM). The optimal thickness and absorbing properties of Ni–Co ferrites were investigated by vector network analyzer (VNA Agilent Technologies E5071C) in the range of 2–18 GHz.

3. Results and discussion

3.1. XRD and TEM characterize

The XRD patterns of the synthesized nanoparticles are shown in Fig. 2. The strong and sharp diffraction peaks from (311) (440) (511) (400) (220) planes reveal the high crystallinity of Ni–Co ferrites and no other impurity peaks could be found. From the SAED analysis, it is obvious that the characteristic of diffraction spots are in line with nickel and cobalt ferrite spinel ferrite, which further validates our test product. After deducting by the JIADE, we found the average size of the particles to be 15 nm, and the lattice strain to be 0.2%. Coupling of the microwave and the milling, which provided significantly high energy, played a critical role in the formation of ferrites.

The TEM pictures illustrated that the Ni–Co ferrite particles (Fig. 3) are very small with an average size around 15 nm. The large amount of nanocrystalline clusters existing in powders have also played an important role in affecting the magnetism properties.

3.2. Magnetism measurements

The magnetic properties of $Ni_xCo_{1-x}Fe_2O_4$ were characterized by VSM, and the results were shown in Table 1. By comparing

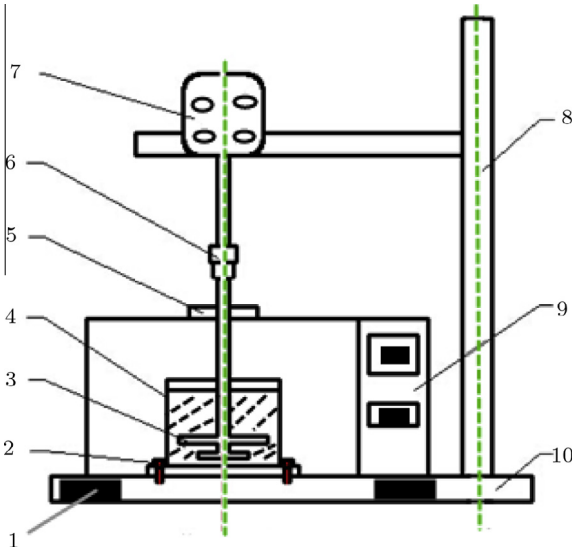

Fig. 1. schematic diagram of the microwave ball-milling device. 1. Fixed base; 2. Bolt; 3. Stirring rod; 4. Milling tank; 5. Radiation protection cover; 6. Universal joint; 7. Motor; 8. Support; 9. Microwave control switch; 10. Closures.

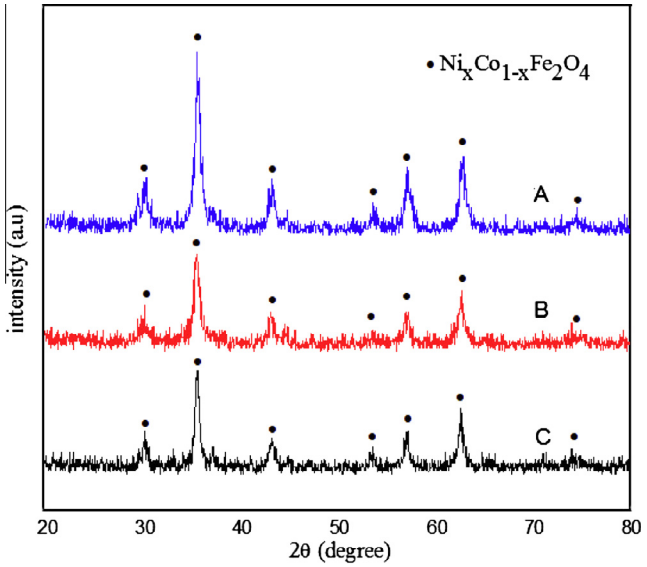

Fig. 2. XRD patterns of $Ni_xCo_{1-x}Fe_2O_4$ ferrites, where *A*, *B*, *C* corresponds to x = 0.2, 0.5, 0.8, respectively.

the experimental data obtained from different processes, the materials prepared by our method presented higher magnetism saturation [28–30], with the values 76 emu/gm, 61 emu/gm and 46 emu/gm respectively. One of the reason for such a noticeable result is the function of mechanical ball milling. Since nano-sized powders generally appeared to have superior magnetic moments compared to bulk phases, this could be highly favorable.

In Table 1, the value of coercivity (H_c) and saturation magnetization (M_s) showed a decrease with the increasing volume of Ni content. This phenomenon could be attributed to two reasons: (1) the synthesized particles are large enough to support the domain walls, and the coercivity (H_c) of nanoparticles could be reduced by magnetization reversal through the domain wall [31]; (2) with the increasing of the x value, the magnetic anisotropy decreases, leading to the easier reversal of moments and a lower H_c value. Then the decrease of M_s. owes to a small magnetic moment of nickle than that of cobalt [32].

3.3. Complex relative permittivity and permeability

There are two major mechanisms responsible for microwave absorbtion: permittivity dispersion and permeability dispersion. They can be directly expressed by real parts μ', ε' and imaginary parts μ'', ε''. In order to study the intrinsic reasons for microwave absorption of the $Ni_xCo_{1-x}Fe_2O_4$, the complex permittivity and permeability were measured and displayed in following Fig. 4. In Fig. 4(a and b), the μ' and μ'' values showed an increase with the decrease of Co concentration in the range of 2–18 GHz. In addition, from Fig. 4(c and d), we noted that the permittivity dispersion also depends upon the Co concentration. Again, the values demonstrate the increasing trend that accompanies a decrease of Co concentration. The reason for this phenomenon is the transferring of electron and hole hopping in Ni–Co ferrites. The increase of a Co element would push away the Ni atom which existed in the A and B sites, as well as the removal of Fe^{3+} from the B site to the A site, and eventually lead to the reducing of electron hopping [33,34]. It is noteworthy that the four pictures exhibited a common feature that the μ', μ'', ε' and ε'' values all tend to be smaller as a whole with an increased frequency. The observed variation can be explained on the space-charge polarization. When the frequency of the applied field is increased, the amount of electrons to go to the boundary