Synthesis and microwave absorbing properties of Cobalt ferrite

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Abstract. Cobalt ferrite powder CoFe₂O₄ was synthesized through the chemical co-precipitation method. The structure, morphology and microwave absorbing properties were studied by changing raw materials, annealing temperature and experimental steps. The measurements of X-ray diffraction and scanning electron micrograph suggest that annealed CoFe₂O₄ sample is still a spinel structure. Moreover, the crystalline and grain sizes become large with the enhancement of annealing temperature. The measurements of microwave absorbing properties show that the reflection loss decreases continuously, and the wavelength of maximum absorption loss shift to short-wave limit as the sample thickness increases.

1. Introduction

Ferrite is a new type of non-metallic magnetic materials, which is quickly developed since 1940s. Currently, it is widely applied to not only in military, but also in the civil aspect, with the development of science and technology, and has become a hot topic in the context of function materials [1-3]. As the composition and structure of ferrite material are different, then their permeability, coercive force and loss of intrinsic magnetism are also various. Therefore, one can prepare ferrite materials with excellent performances by controlling their wide composition and structure.

It is generally known that Cobalt ferrite is a typical ferrite material, which has the unique physical, chemical and magnetic properties. For example, its coercive force and resistivity can achieve the level of dozens of times compared with magnetic alloys [4-6]. The magneto-crystalline anisotropy constant of unit Cobalt ferrite at room temperature can reach 2.7*10⁵ J/m³. The chemical stability is better, abrasion resistant and corrosion stability. Additionally, Cobalt ferrite can still keep high real and imaginary parts of complex permeability at C and Ku wave bands under microwave frequency, which indicates it can produce dielectric loss and magnetic hysteresis loss simultaneously. Therefore, Cobalt ferrite can be used as an important and conventional microwave absorbent [7-9].

In this paper, CoFe₂O₄ particle is synthesized by the chemical co-precipitation method by changing the raw materials, annealing temperatures and experimental steps. Magnetic field annealing is used to controlling and improving the microwave absorption properties. Its composition, phase structure and morphology are characterized by X-ray diffraction (XRD: DX-2000, Cu target, Wavelength 1.54184 Å) and scanning electron micrograph (SEM: JMS-6610 LV). The reflection loss is measured by vector network analyzer (AV3629D).
2. Experiments

CoFe$_2$O$_4$ particle is synthesized by the chemical co-precipitation method based on the following two steps, which are cited as method one and method two for convenience.

Method one: Firstly, Co(CH$_3$COO)$_2$·4H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O were stoichiometrically dissolved in deionized water with Fe/Co=2. Continuously heating when the temperature came to 90 ℃, and then controlling the thermostat and stirred for several minutes. Subsequently, poured into NaOH solution slowly and immediately generated precipitation. After the reaction stopped, and then continuously retained thermal insulation for 40 minutes. Filtrated the gel sediment, washed by deionized water several times until the solution became neutral pH = 7. Finally, it was dried at (100 ±10) ℃ in air and grinded to obtain the precursor of CoFe$_2$O$_4$, the mixture of Co(OH)$_2$ and Fe(OH)$_3$, which was respectively heated to 500 ℃ and 700 ℃ for 2h, and cooled to room temperature.

Method two: CoFe$_2$O$_4$ ferrite nanoparticle was prepared by improved chemical co-precipitation method through boiled in water. Firstly, Co(CH$_3$COO)$_2$·4H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O were stoichiometrically dissolved in deionized water and gently stirred. Secondly, poured the mixture into NaOH solution slowly, stirred for several minutes, stopped heating when the temperature of mixture came to 110 ℃ and lasted this temperature for 2 hours. Thirdly, filtrated the gel sediment and washed by deionized water several times until the solution became neutral. Finally, the mixture was dried at 80 ℃ in air and grinded. In order to prepare monodisperse CoFe$_2$O$_4$ ferrite nanoparticles, CoFe$_2$O$_4$ powder was washed in alcohol, acetone and distilled water, undergone neultrasonic and centrifugal treatment, dried and grined in air.

3. Results and discussion

3.1. Phase structure and morphology

The XRD patterns of CoFe$_2$O$_4$ sample synthesized by the method one with annealing temperature 800 K (denoted by A1) and 1000 K (denoted by A2) are plotted in figure 1. It shows that the samples are spinel structures. Moreover, the strongest diffraction peak appears at crystal plane (311). Therefore, the average grain size of A1 sample calculated by Scherrer formula is about 8.54 nm, and that is about 8.57 nm which corresponds to A2 sample. According to low angle (311) diffraction peak and high angle (400) diffraction peak, one can obtain the lattice constant 8.385 Å by Bragg equation, which well coincides with 8.377 Å reported by Ref. [10].

The XRD patterns of CoFe$_2$O$_4$ sample synthesized by the method two with annealing temperature 400 K (denoted by B1) and 500 K (denoted by B2) are plotted in figure 2. It suggests that diffraction peaks are weaker at lower annealing temperature because of disorderly inter-crystalline structure and nanometer crystal defect result in the continuous change of the lattice space. This indicates that grain is tiny, crystal growth is not complete, and it contains amorphous component. As annealing temperature increases, diffraction peaks become stronger, and CoFe$_2$O$_4$ grain tends to more complete.

Figure 3 (a) and figure 3 (b) plot the SEM images of CoFe$_2$O$_4$ sample synthesized by the method one with annealing temperature 800 K and 1000 K, respectively. Figure 4 (a) and figure 4 (b) also plot the SEM images of CoFe$_2$O$_4$ sample synthesized by method two with annealing temperature 400 K and 500 K, respectively. The elaborate comparisons between different methods and annealing temperature are rather obviously. It can be seen that the morphology of pure CoFe$_2$O$_4$ is relatively homogeneous rod with the diameter in micron scale. Moreover, the average grain size of CoFe$_2$O$_4$ nanoparticles synthesized by the same method continuously increases as annealing temperature increases. It shows that there exists obvious aggregation. As the average grain size of CoFe$_2$O$_4$ nanoparticles is too small and the distance between particles is short, and then the van der Waals force is greater than the gravity, which leads to an aggregation, even crowds or masses into a dense cluster [11, 12], as shown in figure 4.
Figure 1. XRD patterns of CoFe$_2$O$_4$ synthesized by the method one by annealing temperature 800 K (denoted by A1) and 1000 K (denoted by A2).

Figure 2. XRD patterns of CoFe$_2$O$_4$ synthesized by the method two by annealing temperature 400 K (denoted by B1) and 500 K (denoted by B2).

Figure 3. SEM images of CoFe$_2$O$_4$ synthesized by the method one at different annealing temperatures.
3.2. Microwave absorbing properties
To obtain the reflection loss, one should mix the samples and paraffin wax with ratio 1: 1, poured the mixtures into a beaker into oven, heated to 80 °C for several minutes, put them into a coaxial cylinder, pressed into annulations with inner diameter 3.04 mm, outside diameter 7.00 mm, and thickness 1-3 mm.

Figure 5(a) and figure 5(b) are the curves of reflection loss versus frequency of CoFe$_2$O$_4$ and paraffin wax mixtures synthesized by the method one with different thicknesses at annealing temperature 800 K and 1000 K, respectively. As shown in figure 5, the change trends and reflection loss degree of CoFe$_2$O$_4$ sample with same thickness and different annealing temperatures are basically similar. The main reason of reflection loss lies in that the change in magnetization lags behind the magnetic field. When the responses of magnetic domain rotation or domain wall displacement lag behind the variation under external magnetic field annealing process, it will produce a large loss. It can be seen that the degree of reflection loss decreases as the sample thickness (2-3mm) increases. Moreover, the wavelength of maximum absorption loss tends to the direction of low frequency and short-wave limit [10]. The reflection loss changes significantly and the maximum absorption peak of the samples can reach to -48 dB, which appears at about 14.5 GHz with a thickness of 2 mm. These results suggest that it is easier to improve microwave absorbing performance through magnetic field annealing. Further experiments demonstrate that the same conclusions can also been obtained by the sample synthesized by the method two.

Figure 5. Reflection loss versus frequency of CoFe$_2$O$_4$ synthesized by the method one with different thicknesses: (a) annealing temperature 800 K, (b) annealing temperature 1000 K.
4. Conclusions
We have successfully prepared the light-weight and strong absorption microwave absorber CoFe$_2$O$_4$ by using chemical co-precipitation method. It is suggested that CoFe$_2$O$_4$ ferrite is still a spinel structure based on different annealing temperatures. The crystalline and grain sizes become large as annealing temperature increases. Our results also show that the reflection loss decreases along with the enhancement of sample thickness. Moreover, the wavelength of maximum absorption loss tends to the direction of short-wave limit. Annealing is advantageous to the improvement of absorbing properties.

Acknowledgements
This work is supported by the natural science foundation of Shandong province (No. ZR2017MEM012) and the technology program for doctor of Heze University (No. XY16BS32).

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